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LA THÈSE A ÉTÉ
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STABLE VARIATIONAL SOLUTIONS OF THE DIRAC EQUATION

by

Sydney John Peel

Submitted to the
Faculty of Graduate Studies and Research
through the
Department of Physics
in partial fulfillment
of the requirements for the
Degree of Master of Science
at the University of Windsor

Windsor, Ontario, Canada

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Abstract

Recent proposals for the solution of relativistic many-electron problems and their concomitant inadequacies are discussed. The solution of the Dirac equation through the application of the Ritz variational method to the square of the Dirac Hamiltonian is then outlined and the results of the implementation of this method in certain variational subspaces is presented. Derivations of several relativistic sum rules are included for completeness.

The eigenenergies obtained from the method are in excellent agreement with the analytic values, while there is a considerable discrepancy in several of the sum rules, arising from the unavoidable use of finite-dimensional variational subspaces. However, the behaviour of certain of the sum rules would indicate that the lower-lying eigenstates are in good agreement with their analytic counterparts.

More reliable tests of the quality of the variational wavefunctions and applications of the method to relativistic molecular calculations are suggested.

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Introduction

The spectrum of the Dirac Hamiltonian has no lower bound and the Dirac Hamiltonian therefore eludes the Hylleraas-Undheim Theorem^{1,8} which guarantees that the approximations, obtained through the Ritz variational method, to the eigenvalues of an operator whose spectrum is bounded from below can be no smaller than those eigenvalues. Consequently, relativistic treatments of both one- and many-electron systems based on variational methods are often subject to severe instabilities.

These instabilities have been subject to two principal classifications²: the Brown-Ravenhall disease and inadequate representation of the kinetic energy operator $\vec{\alpha} \cdot \vec{p}$ in the Dirac Hamiltonian. The Brown-Ravenhall disease^{3,4,5} arises from the absence of bound-state solutions to a relativistic many-electron Hamiltonian incorporating electron-electron interactions, and thus will not affect one-electron problems. The inadequate representation of the kinetic energy operator, on the other hand, will affect both one- and many-electron calculations.

In applying the variational method the variational solutions tend to collapse to the continuum of negative energy states and thus one approach to the solution of the Dirac-Hartree-Fock equations is to project out these negative energy states. While this procedure has met with success in the treatment of atomic systems, progress in the treatment of molecular systems has been rather limited.

Mark and Schwarz⁶ address the instability due to inadequate representation of the kinetic energy operators by modifying this representation. While their method does give the exact ground-state

eigenenergies for a four-dimensional variational subspace, the corresponding eigenfunctions, particularly for large atomic numbers, can deviate considerably from the actual eigenfunctions. In addition the method gives incorrect results for positrons in the non-relativistic limit if it is required to yield the actual values for electrons in the same limit. Aside from the above considerations, a generalized Hylleraas-Undheim Theorem has not been proven for the method.

By a proutious choice of their variational subspace Drake and Goldman have successfully applied the Ritz variational method to the Dirac Hamiltonian to obtain the eigenenergies and eigenfunctions of a hydrogenic system. The method gives extremely good results and the actual eigenenergies are lower bounds of the variational eigenenergies obtained. However, a generalized Hylleraas-Undheim Theorem has been proven only for a two-dimensional variational subspace and in fact for $K > 0$ a clearly extraneous eigenenergy is obtained which lies below the actual ground-state eigenenergy. The result of the application of the technique to non-hydrogenic potentials is unclear and indeed the radial dependence of the potential appears to be rather crucial to the proof of the generalized Hylleraas-Undheim Theorem for the two-dimensional variational subspace advanced by Drake and Goldman. In addition, while for a two-dimensional variational subspace their method yields the correct ground state eigenenergy, the corresponding eigenfunction is determined only up to a function giving the correct expectation of r^{-1} .

An alternative to the above methods is the application of the Ritz variational method to the square of the Dirac Hamiltonian, an approach apparently first proposed by Hallmeier and Kutzelnigg.⁹

The square of the Dirac Hamiltonian is clearly positive definite and thus succumbs to the Hylleraas-Undheim Theorem. It only remains to extract approximations to the spectrum and corresponding eigenfunctions of the Dirac Hamiltonian from the variational solutions obtained for the squared Dirac Hamiltonian.

In this paper we sketch an outline of the relevant aspects of the Dirac equation and the Ritz variational method, along with a derivation of the relativistic sum rules employed as a measure of the quality of the variational basis. The method of Drake and Goldman and that advocated here are then compared for a two-dimensional variational subspace, and subsequently implementation of Wallmeier and Kutzelnigg's method for generalized Slater-type orbital bases of arbitrary dimension is outlined. We include as an appendix an analysis of the Mark-Schwarz method for a four-dimensional variational subspace.

The Dirac Equation^{10,11}

A relativistic quantum-mechanical description of an electron in the presence of an external field described by the scalar potential V and the vector potential \vec{A} is realized in the Dirac equation

$$(\vec{\alpha} \cdot \vec{p} + mc^2 \beta + V) \psi = i\hbar \frac{\partial \psi}{\partial t} \quad (1)$$

where $\vec{p} = -i\hbar \nabla - e/c \vec{A}$ and the operators $\vec{\alpha}, \beta$ are independent of the spacetime coordinates and satisfy the anticommutator relations

$$\{\alpha_k, \alpha_l\} = 2\delta_{kl}$$

$$\{\beta, \beta\} = 2$$

$$\{\alpha_k, \beta\} = 0$$

It can be shown from the above relations that the space upon which the $\vec{\alpha}, \beta$ operate must have an even dimension and in fact a four-dimensional space affords an irreducible representation of the state space of the system. The four components of the wavefunction in this space represent the two possible energy states of the electron and the two possible spin states in each of these energy states. Explicit representations of the $\vec{\alpha}, \beta$ are given by

$$\alpha_k = \begin{pmatrix} 0 & \vec{\sigma}_k \\ \vec{\sigma}_k & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

where the $\vec{\sigma}_k$ are the Pauli spin matrices.

Owing to the time-independence of the $\vec{\alpha}, \beta$ it is apparent that (1) possesses stationary solutions

$$\psi(\vec{r}, t) = \psi(\vec{r}) e^{-iE/\hbar t} \quad (2)$$

for static external fields, in which case it reduces to

$$H_0 \psi(\vec{r}) = E \psi(\vec{r}) \quad (3)$$

where H_0 is the Dirac Hamiltonian given by

$$H_0 = -i\hbar c \vec{\alpha} \cdot \vec{\nabla} + mc^2 \beta + V \quad (4)$$

If in addition the potentials satisfy

$$V = V(r)$$

$$\vec{A} = \vec{0}$$

then a separation of variables can be effected in (3) analogous to the separation of radial and angular dependencies in the Schrodinger equation for a spherically symmetric system. In particular, the eigenstates of (4) have the form

$$\psi_{jkm_f} = \begin{pmatrix} g(r) u_{f,l}^{m_f} \\ i f(r) u_{f,l}^{m_f} \end{pmatrix}, \quad \tilde{l} \equiv 2j - l \\ \kappa \equiv \frac{1}{2}(l(l+1) - \tilde{l}(\tilde{l}+1)) \quad (5)$$

where the $u_{f,l}^{m_f}$ is an extension of the spherical harmonic and is defined by²⁰

$$u_{f,l}^{m_f} = \langle l m_l \frac{1}{2} m_s | j m_f \rangle Y_l^{m_l}(\hat{r}) \chi^{m_s} \quad (6)$$

with

$$\chi^{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi^{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The $u_{f,l}^{m_f}$ are simultaneous eigenfunctions of J^2 , J_z , L^2 and S^2 corresponding to the eigenvalues $j(j+1)\hbar^2$, $m_f\hbar$, $l(l+1)\hbar^2$ and $s(s+1)\hbar^2$ respectively, where \vec{J} is the total angular momentum:

$$\vec{J} = \vec{L} + \vec{S}, \quad \vec{S} \equiv \frac{1}{2} \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}$$

The $Y_l^{m_l}$ are eigenfunctions of L^2 and L_z , \vec{L} being the orbital angular momentum, whence the appearance of the Clebsch-Gordan

coefficients in (6). These extended spherical harmonics also satisfy the normalization condition

$$\int_{4\pi} \psi_{j\ell}^{m_i\dagger}(\hat{r}) \psi_{j'\ell'}^{m_i'}(\hat{r}) d\Omega = \delta_{jj'} \delta_{\ell\ell'} \delta_{m_i m_i'}$$

Observe that the spin-angular dependence of the eigenfunction is confined to these extended spherical harmonics, the two explicit components of the eigenfunctions in (5) representing the two energy states of the electron.

Substitution of (5) for ψ in (3) yields the system of two coupled first-order differential equations

$$\frac{dq}{dr} = -\frac{\kappa}{r} q + \frac{1}{\hbar c} (E + mc^2 - V) f$$

$$\frac{df}{dr} = \frac{1}{\hbar c} (E - mc^2 + V) q + \frac{\kappa}{r} f$$

which become for a hydrogenic system ($V = -\frac{Ze^2}{r}$)

$$\frac{dq}{dr} = -\frac{\kappa}{r} q + \left\{ \frac{1}{\hbar c} (E + mc^2) + \frac{Ze}{r} \right\} f$$

$$\frac{df}{dr} = -\left\{ \frac{1}{\hbar c} (E - mc^2) + \frac{Ze}{r} \right\} q + \frac{\kappa}{r} f$$

The solution of this system is facilitated by the transformation

$$q(r) = \left(\frac{1}{\hbar c} (mc^2 + E) \right)^{1/2} e^{-\lambda r} (\phi_1 + \phi_2)$$

$$f(r) = \left(\frac{1}{\hbar c} (mc^2 - E) \right)^{1/2} e^{-\lambda r} (\phi_1 - \phi_2)$$

$$\lambda \equiv \frac{1}{\hbar c} ((mc^2)^2 - E^2)^{1/2}$$

Upon effecting this transformation the system can be solved by

making the substitutions

$$\phi_1(x) = x^\gamma \sum_{m=0}^{\infty} a_m x^m$$

$$\phi_2(x) = x^\gamma \sum_{m=0}^{\infty} b_m x^m$$

$$x \equiv 2\lambda r$$

where at least one of a_0, b_0 is non-zero. The resulting equations are then solved for γ and for the a_m, b_m in terms of a_0 , which is itself obtained by requiring the solutions to be normalized.

$$i.e. \langle \psi_{l, m_f} | \psi_{l', m_f'} \rangle = \int_{4\pi} \int_0^\infty (r q(r) u_{l, l'}^{m_f, m_f'}(r) - r f(r) u_{l, l'}^{m_f, m_f'}(r)) \left(\frac{r q(r) u_{l, l'}^{m_f, m_f'}(r)}{r f(r) u_{l, l'}^{m_f, m_f'}(r)} \right) r^2 dr d\Omega$$

$$= 1$$

In this manner the radial components of a bound eigenstate are obtained as

$$q(r) = - \left(\frac{1}{\hbar c} (mc^2 + E) \right)^{\frac{1}{2}} e^{-\lambda r} (d_1(2\lambda r) + d_2(2\lambda r))$$

$$f(r) = \left(\frac{1}{\hbar c} (mc^2 - E) \right)^{\frac{1}{2}} e^{-\lambda r} (d_1(2\lambda r) - d_2(2\lambda r))$$

where

$$d_1(x) = a_0 x^\gamma F(1-n', 2\gamma+1, x) \quad (7)$$

$$d_2(x) = a_0 \frac{\kappa - \frac{3\lambda mc^2}{\hbar c \lambda}}{n'} F(-n', 2\gamma+1, x) \quad (8)$$

with

$$\gamma = (\kappa^2 - (3\lambda)^2)^{\frac{1}{2}}$$

$$\lambda = \frac{3\lambda}{|\kappa|} \frac{mc}{\hbar} \left(1 + \frac{n'}{\kappa} \left(\frac{n'}{\kappa} + 2 \right) \right)^{-\frac{1}{2}}$$

$$a_0 = - \frac{\lambda}{\Gamma(2\gamma+1)} \left(\frac{\Gamma(2\gamma+n'+1)}{2\lambda \hbar c \left(\frac{3\lambda \hbar c}{\lambda} - \kappa \right) n'} \right)^{\frac{1}{2}}$$

and n' is a non-negative integer (representing the number of nodes of $g(r)$), which condemns the confluent hypergeometric functions in (7), (8) to be polynomials in $2\lambda r$. Thus we can express the radial components in the somewhat more explicit form

$$q(r) = -a_0 (mc^2 + E)^{\frac{1}{2}} r^{\gamma-1} e^{-\lambda r} \sum_{m=0}^{n'} \frac{(2\lambda)^m}{\prod_{i=1}^m (2\gamma+i)} (-1)^{m+1} \left\{ n' \binom{n'-1}{m} + \left(\kappa - \frac{3\lambda \hbar c}{\lambda} \right) \binom{n'}{m} \right\} r^m$$

$$f(r) = -a_0 (mc^2 - E)^{\frac{1}{2}} r^{\gamma-1} e^{-\lambda r} \sum_{m=0}^{n'} \frac{(2\lambda)^m}{\prod_{i=1}^m (2\gamma+i)} (-1)^m \left\{ n' \binom{n'-1}{m} - \left(\kappa - \frac{3\lambda \hbar c}{\lambda} \right) \binom{n'}{m} \right\} r^m$$

The corresponding eigenenergies are given by

$$E_{n,j} = mc^2 \left(1 + \left(\frac{Z\alpha}{n' + (j + \frac{1}{2}) - (Z\alpha)^2 \frac{1}{2}} \right)^2 \right)^{-\frac{1}{2}} = mc^2 \left(1 + \left(\frac{Z\alpha}{n' + j} \right)^2 \right)^{-\frac{1}{2}} \quad (10)$$

In addition to this bound-state discrete region the spectrum of the Dirac Hamiltonian for a hydrogenic system includes the continua

$$(-\infty, -mc^2) \quad \text{and} \quad (mc^2, \infty).$$

Relativistic Sum Rules^{12,13}

Denoting the eigenstates of H_0 corresponding to the eigen-energy E_s of H_0 by $|\psi_s\rangle$ the sum rules referred to in this paper are expressions for the quantities

$$S_R \equiv \frac{2}{3} \left\{ \sum_{0 \leq E_s < mc^2} (E_s - E_0)^R |\langle \psi_0 | \vec{r} | \psi_s \rangle|^2 + \int_{|E_s| > mc^2} \rho(E_s) (E_s - E_0)^R |\langle \psi_0 | \vec{r} | \psi_s \rangle|^2 dE_s \right\} \quad (11)$$

$R \in \mathbb{N}_0$

in terms of the expectations of certain operators in the state $|\psi_0\rangle$

where $|\psi_0\rangle$ is one of the bound-state eigenfunctions of the Hamiltonian and ρ gives the density of the states in momentum space. Since these expectations can be calculated analytically for hydrogenic systems the sum rules can thus be employed as a measure of the quality of the variational basis employed. In the following we shall tacitly include the integrations over the continua performed in the second term of (11) in the summation of the first term; i.e., we rewrite (11) as

$$S_R = \frac{2}{3} \sum_s (E_s - E_0)^R |\langle \psi_0 | \vec{r} | \psi_s \rangle|^2 \quad (12)$$

We now proceed to obtain the afore-mentioned expectation, after the manner of Goldman.¹²

Since H_0 is an observable and its eigenstates must therefore span the state space it follows immediately that

$$\begin{aligned} S_0 &= \frac{2}{3} \sum_s |\langle \psi_0 | \vec{r} | \psi_s \rangle|^2 \\ &= \frac{2}{3} \sum_s \langle \psi_0 | \vec{r} | \psi_s \rangle \langle \psi_s | \vec{r} | \psi_0 \rangle \\ &= \frac{2}{3} \langle \psi_0 | r^2 | \psi_0 \rangle \end{aligned}$$

For S_1 we observe that

$$\begin{aligned} S_1 &= \frac{2}{3} \sum_s (E_s - E_0) |\langle \psi_0 | \vec{r} | \psi_s \rangle|^2 \\ &= \frac{2}{3} \sum_s (E_s - E_0) \langle \psi_0 | \vec{r} | \psi_s \rangle \cdot \langle \psi_s | \vec{r} | \psi_0 \rangle \\ &= \frac{2}{3} \sum_s \langle \psi_0 | [\vec{r}, H] | \psi_s \rangle \cdot \langle \psi_s | \vec{r} | \psi_0 \rangle \quad (13) \end{aligned}$$

and similarly

$$\begin{aligned} S_1 &= \frac{2}{3} \sum_S \langle \psi_0 | \vec{r} | \psi_S \rangle \cdot \langle \psi_S | [H, \vec{r}] | \psi_0 \rangle \\ &= -\frac{2}{3} \sum_S \langle \psi_0 | \vec{r} | \psi_S \rangle \cdot \langle \psi_S | [\vec{r}, H] | \psi_0 \rangle \end{aligned} \quad (14)$$

where we have employed the fact that ψ_0, ψ_S are eigenstates of H_0 .

Adding (13) and (14) and invoking the completeness of the eigenstates of H_0 gives us

$$S_1 = \frac{1}{3} \langle \psi_0 | [[\vec{r}, H]; \vec{r}] | \psi_0 \rangle$$

But for $H = c\vec{\alpha} \cdot \vec{p} + mc^2\beta + V(\vec{r})$ it follows that

$$[\vec{r}, H] = c\vec{\alpha} \cdot [\vec{r}, \vec{p}] = i\hbar c\vec{\alpha}$$

$$\Rightarrow [[\vec{r}, H]; \vec{r}] = i\hbar c[\vec{\alpha}; \vec{r}] = 0$$

and thus we have that $S_1 = 0$.

$$\begin{aligned} S_2 &\equiv \frac{2}{3} \sum_S (E_S - E_0)^2 |\langle \psi_0 | \vec{r} | \psi_S \rangle|^2 \\ &= -\frac{2}{3} \sum_S (E_S - E_0) \langle \psi_0 | \vec{r} | \psi_S \rangle (E_0 - E_S) \langle \psi_S | \vec{r} | \psi_0 \rangle \\ &= -\frac{2}{3} \sum_S \langle \psi_0 | [\vec{r}, H] | \psi_S \rangle \cdot \langle \psi_S | [\vec{r}, H] | \psi_0 \rangle \\ &= -\frac{2}{3} \langle \psi_0 | [\vec{r}, H]^2 | \psi_0 \rangle \\ &= -\frac{2}{3} \langle \psi_0 | (-i\hbar c\vec{\alpha})^2 | \psi_0 \rangle \\ &= 2\hbar^2 c^2 \end{aligned}$$

Noting that

$$\begin{aligned} \langle \psi_S | [H, [H, \vec{r}]] | \psi_0 \rangle &= \langle \psi_S | H^2 \vec{r} - 2H \vec{r} H + \vec{r} H^2 | \psi_0 \rangle \\ &= (E_S - E_0)^2 \langle \psi_S | \vec{r} | \psi_0 \rangle \end{aligned}$$

we have for S_3

$$\begin{aligned} S_3 &\equiv \frac{2}{3} \sum_S (E_S - E_0)^3 \\ &= \frac{2}{3} \sum_S (E_S - E_0) \langle \psi_0 | \vec{r} | \psi_S \rangle (E_S - E_0)^2 \langle \psi_S | \vec{r} | \psi_0 \rangle \\ &= \frac{2}{3} \sum_S \langle \psi_0 | [\vec{r}, H] | \psi_S \rangle \cdot \langle \psi_S | [H, [H, \vec{r}]] | \psi_0 \rangle \end{aligned} \quad (15)$$

and similarly

$$\begin{aligned}
 S_3 &= \frac{2}{3} \sum_s \langle \psi_0 | [H, [H, \vec{r}]] | \psi_s \rangle \langle \psi_s | [H, \vec{r}] | \psi_0 \rangle \\
 &= -\frac{2}{3} \sum_s \langle \psi_0 | [H, [H, \vec{r}]] | \psi_s \rangle \langle \psi_s | [\vec{r}, H] | \psi_0 \rangle
 \end{aligned} \tag{16}$$

Adding (15) and (16) gives us

$$S_3 = \frac{1}{3} \langle \psi_0 | [[\vec{r}, H]; [H, [H, \vec{r}]] | \psi_0 \rangle$$

and

$$\begin{aligned}
 [H, [H, \vec{r}]] &= i\hbar c [\vec{z}, H] \\
 &= i\hbar c [\vec{z}, i\hbar c \vec{z} \cdot \nabla + mc^2 \beta] \\
 &= -(\hbar c)^2 [\vec{z}, \vec{z}] \cdot \nabla + i\hbar mc^3 [\vec{z}, \beta] \rightarrow 0 \\
 &= 2(\hbar c)^2 i \epsilon_{klm} \Sigma_m \frac{\partial}{\partial x_l} \hat{e}_k + 2i\hbar mc^3 \vec{z} \beta
 \end{aligned}$$

$$\begin{aligned}
 \Rightarrow [[\vec{r}, H]; [H, [H, \vec{r}]]] &= i\hbar c [\vec{z}; [H, [H, \vec{r}]]] \\
 &= i\hbar c [\epsilon_k, 2(\hbar c)^2 i \epsilon_{klm} \Sigma_m \frac{\partial}{\partial x_l} \hat{e}_k + [\epsilon_k, 2i\hbar mc^3 \epsilon_k \beta]] \\
 &= -2(\hbar c)^3 \epsilon_{klm} [\epsilon_k, \Sigma_m] \frac{\partial}{\partial x_l} - 2\hbar^2 mc^4 [\epsilon_k, \epsilon_k \beta] \\
 &= -4(\hbar c)^3 \epsilon_{klm} (i\epsilon_{kln} \epsilon_n) \frac{\partial}{\partial x_l} - 4\hbar^2 mc^4 \delta_{kk} \beta \\
 &= 8(\hbar c)^3 i \vec{z} \cdot \nabla - 12\hbar^2 mc^4 \beta
 \end{aligned}$$

$$\therefore S_3 = \frac{8}{3} (\hbar c)^3 i \langle \psi_0 | \vec{z} \cdot \nabla | \psi_0 \rangle - 4(\hbar c)^2 \langle \psi_0 | mc^2 \beta | \psi_0 \rangle \tag{17}$$

But from (4) we have that

$$\hbar c^2 \beta = H_0 + i\hbar c \vec{r} \cdot \nabla - V$$

giving us

$$S_3 = \frac{4}{3}(\hbar c)^3 \langle \psi_0 | -i\hbar c \vec{r} \cdot \nabla | \psi_0 \rangle - 4(\hbar c)^2 \langle \psi_0 | H_0 | \psi_0 \rangle + 4(\hbar c)^2 \langle \psi_0 | V | \psi_0 \rangle$$

so that (17) can be written

$$S_3 = \frac{4}{3}(\hbar c)^2 \langle \psi_0 | -i\hbar c \vec{r} \cdot \nabla | \psi_0 \rangle - 4(\hbar c)^2 E_0 + 4(\hbar c)^2 \langle \psi_0 | V | \psi_0 \rangle$$

and

$$\begin{aligned} [H, \vec{r} \cdot \nabla] &= [-i\hbar c \vec{r} \cdot \nabla, \vec{r} \cdot \nabla] + [V(\vec{r}), \vec{r} \cdot \nabla] \\ &= c \vec{r} \cdot [\vec{p}, \vec{r}] \cdot \nabla + \vec{r} \cdot [V(\vec{r}), \nabla] \\ &= -i\hbar c \vec{r} \cdot \nabla - \vec{r} \cdot (\nabla V) \end{aligned}$$

$$\begin{aligned} \Rightarrow S_3 &= \frac{4}{3}(\hbar c)^2 \{ \langle \psi_0 | [H, \vec{r} \cdot \nabla] | \psi_0 \rangle + \langle \psi_0 | \vec{r} \cdot (\nabla V) | \psi_0 \rangle \} - 4E_0 + 4 \langle \psi_0 | V | \psi_0 \rangle \\ &= \frac{4}{3}(\hbar c)^2 \langle \psi_0 | \vec{r} \cdot (\nabla V) | \psi_0 \rangle - 4(\hbar c)^2 E_0 + 4(\hbar c)^2 \langle \psi_0 | V | \psi_0 \rangle \end{aligned}$$

$$S_4 = \frac{2}{3} \sum_S (E_S - E_0)^4 |\langle \psi_0 | \vec{r} | \psi_S \rangle|^2$$

$$= \frac{2}{3} \sum_S (E_S - E_0)^2 \langle \psi_0 | \vec{r} | \psi_S \rangle \cdot (E_S - E_0)^2 \langle \psi_S | \vec{r} | \psi_0 \rangle$$

$$= \frac{2}{3} \sum_S \langle \psi_0 | [H, [H, \vec{r}]] | \psi_S \rangle \cdot \langle \psi_S | [H, [H, \vec{r}]] | \psi_0 \rangle$$

$$= \frac{2}{3} \langle \psi_0 | [H, [H, \vec{r}]] ; [H, [H, \vec{r}]] | \psi_0 \rangle$$

$$\text{and } \{[H, [H, \hat{r}]]; [H, [H, \hat{r}]]\}^{13}$$

$$= \{2(\hbar c)^3 i \epsilon_{ijk} \Sigma_k \frac{\partial}{\partial x_j} + 2i \hbar m c^2 \alpha_i \beta, 2(\hbar c)^3 i \epsilon_{ilm} \Sigma_m \frac{\partial}{\partial x_l} + 2i \hbar m c^2 \alpha_i \beta\}$$

$$= -4(\hbar c)^4 \epsilon_{ijk} \epsilon_{ilm} [\Sigma_k, \Sigma_m] \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_l} - 8(\hbar c)^3 m c^2 \epsilon_{ilm} \{\alpha_i \beta, \Sigma_m\} \frac{\partial}{\partial x_l} \\ - 4(\hbar c)^2 (m c^2)^3 \{\alpha_i \beta, \alpha_i \beta\}$$

$$= -8(\hbar c)^4 \epsilon_{ijk} \epsilon_{ilm} \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_l} - 8(\hbar c)^3 m c^2 \epsilon_{ilm} (\{\alpha_i, \Sigma_m\} \beta + \alpha_i [\beta, \Sigma_m] \frac{\partial}{\partial x_l}) \\ - 4(\hbar c)^2 (m c^2)^3 (\{\alpha_i, \alpha_i \beta\} + \alpha_i [\beta, \alpha_i \beta])$$

$$= -16(\hbar c)^4 \nabla^2 - 4(\hbar c)^2 (m c^2)^3 (\{\alpha_i \beta, \alpha_i\} - [\alpha_i, \alpha_i] \beta + \alpha_i [\beta, \alpha_i] \beta)$$

$$= -16(\hbar c)^4 \nabla^2 + 8(\hbar c)^2 (m c^2)^2 \vec{\alpha} \cdot \vec{\alpha} \beta^2$$

$$= -16(\hbar c)^4 \nabla^2 + 24(\hbar c)^2 (m c^2)^2$$

$$\Rightarrow S_4 = -1/3 (\hbar c)^4 \nabla^2 + 24(\hbar c)^2 (m c^2)^2$$

$$\text{For a Coulomb field } V(r) = -\frac{Z e^2 \hbar c}{r} \Rightarrow \vec{r} \cdot \nabla V = -V$$

and we can summarize the above relations as

$$S_0 = \langle \psi_0 | r^2 | \psi_0 \rangle$$

$$S_1 = 0$$

$$S_2 = 2(\hbar c)^2$$

$$S_3 = -(\hbar c)^2 \left\{ \frac{8}{3} Z e^2 \hbar c \langle \psi_0 | r^{-1} | \psi_0 \rangle + 4 E_0 \right\}$$

$$S_4 = (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{16}{3} (\hbar c)^2 \langle \psi_0 | \nabla^2 | \psi_0 \rangle \right\}$$

In addition to the above sum rules we also have for the dipole polarizability:

$$\alpha = S_{-1}$$

Taking ψ_0 to be the ground-state eigenfunction

$$\text{i.e. } \psi_0 = \begin{pmatrix} \frac{1}{2} q(r) \chi_{\frac{1}{2} 0}^m \\ \frac{1}{2} f(r) \chi_{\frac{1}{2} 1}^m \end{pmatrix}$$

$$\text{where } q(r) = b_0 r^\gamma e^{-\lambda r}, \quad b_0 = \left(\frac{1+\gamma}{\Gamma(2\gamma+1)} \lambda \right)^{\frac{1}{2}} (2\lambda)^\gamma$$

$$f(r) = - \left(\frac{1-\gamma}{1+\gamma} \right)^{\frac{1}{2}} q(r).$$

$$\gamma = (1 - (z\alpha)^2)^{\frac{1}{2}}$$

$$\lambda = z\alpha \frac{mc}{\hbar}$$

with corresponding eigenenergy

$$E_0 = \gamma mc^2$$

we have for S_0 , S_3 , and S_4 :

$$S_0 = \langle \psi_0 | r^2 | \psi_0 \rangle$$

$$= \left(1 + \frac{1-\gamma}{1+\gamma} \right) \langle q | r^2 | q \rangle$$

$$= \frac{2}{1+\gamma} \frac{1+\gamma}{\Gamma(2\gamma+1)} \lambda (2\lambda)^{2\gamma} \int_0^\infty r^{2\gamma+2} e^{-2\lambda r} dr$$

$$= 2\lambda \frac{(2\gamma+2)\Gamma(2\gamma+1)}{(2\lambda)^3}$$

$$= \frac{(\gamma+1)(\gamma+\frac{1}{2})}{\lambda^2}$$

$$\begin{aligned}
S_3 &= -(\hbar c)^2 \left\{ \frac{8}{3} \frac{Z}{\lambda} \hbar c \langle \psi_0 | r^{-1} | \psi_0 \rangle + 4 \gamma m c^2 \right\} \\
&= -(\hbar c)^2 \left\{ \frac{8}{3} \frac{Z}{\lambda} \hbar c \left(1 + \frac{1-\gamma}{1+\gamma} \right) \langle q | r^{-1} | q \rangle + 4 \gamma m c^2 \right\} \\
&= -(\hbar c)^2 \left\{ \frac{16}{3} \frac{Z \hbar c}{1+\gamma} b_0^2 \int_0^\infty r^{2\gamma-1} e^{-2\lambda r} dr + 4 \gamma m c^2 \right\} \\
&= -(\hbar c)^2 \left\{ \frac{16}{3} \frac{Z \hbar c}{1+\gamma} \frac{1+\gamma}{\Gamma(2\gamma+1)} (2\lambda)^{2\gamma} \frac{\Gamma(2\gamma)}{(2\lambda)^{2\gamma}} + 4 \gamma m c^2 \right\} \\
&= -(\hbar c)^2 \left\{ \frac{8}{3} \frac{Z \hbar c}{\gamma} + 4 \gamma m c^2 \right\}
\end{aligned}$$

$$\begin{aligned}
S_4 &= (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{16}{3} (\hbar c)^2 \langle \psi_0 | \nabla^2 | \psi_0 \rangle \right\} \\
&= (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{16}{3} (\hbar c)^2 \left\langle \begin{pmatrix} \frac{1}{r} q(r) \psi_{\frac{1}{2},0}^\gamma \\ \frac{1}{r} f(r) \psi_{\frac{1}{2},1}^\gamma \end{pmatrix} \left| \frac{\partial^2}{\partial r^2} r - \frac{\lambda^2}{r^2} \right| \begin{pmatrix} \frac{1}{r} q(r) \psi_{\frac{1}{2},0}^\gamma \\ \frac{1}{r} f(r) \psi_{\frac{1}{2},1}^\gamma \end{pmatrix} \right\rangle \right\} \\
&= (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{16}{3} (\hbar c)^2 \left[\left(1 + \frac{1-\gamma}{1+\gamma} \right) \langle q | \frac{\partial^2}{\partial r^2} | q \rangle - \frac{1-\gamma}{1+\gamma} \langle q | r^{-2} | q \rangle \right] \right\} \\
&= (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{32}{3} \frac{(\hbar c)^2}{1+\gamma} b_0^2 \left[\int_0^\infty r^\gamma e^{-\lambda r} \frac{\partial^2}{\partial r^2} r^\gamma e^{-\lambda r} dr - (1-\gamma) \int_0^\infty r^{2\gamma-2} e^{-2\lambda r} dr \right] \right\} \\
&= (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{32}{3} \frac{(\hbar c)^2}{1+\gamma} \frac{1+\gamma}{\Gamma(2\gamma+1)} \lambda (2\lambda)^{2\gamma} \left[(\gamma^2-1) \frac{\Gamma(2\gamma-1)}{(2\lambda)^{2\gamma-1}} \right. \right. \\
&\quad \left. \left. - 2\lambda \frac{\Gamma(2\gamma)}{(2\lambda)^{2\gamma}} + \lambda^2 \frac{\Gamma(2\gamma+1)}{(2\lambda)^{2\gamma+1}} \right] \right\} \\
&= (\hbar c)^2 \left\{ 8(m c^2)^2 - \frac{32}{3} (\hbar c \lambda)^2 \left[\frac{\gamma^2-1}{\gamma(2\gamma-1)} - \frac{\gamma}{2} \right] \right\} \\
&= 8(\hbar c)^2 \left\{ (m c^2)^2 - \frac{2}{3} (\hbar c \lambda)^2 \frac{\gamma-2}{\gamma(2\gamma-1)} \right\}
\end{aligned}$$

The Ritz Variational Method⁵

The Ritz variational method of obtaining the discrete eigen-energies and corresponding eigenstates of a Hamiltonian consists of introducing an appropriate subset \mathcal{V} (the variational subset) of the state space \mathcal{E} of H and determining those elements of \mathcal{V} for which the functional $E: \mathcal{E} - \{0\} \rightarrow \mathbb{C}$ defined by

$$E(\psi) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (\forall \psi \in \mathcal{E} - \{0\})$$

is stationary. (Observe that E is independent of the normalization of $|\psi\rangle$.)

The equivalence of this optimization of E to the original eigen-value problem can be demonstrated as follows. The variation of E with an arbitrary variation $|\delta\psi\rangle$ of $|\psi\rangle$ is given by

$$\begin{aligned} \langle \psi | \psi \rangle \delta E + E \{ \langle \delta\psi | \psi \rangle + \langle \psi | \delta\psi \rangle \} &= \langle \delta\psi | H | \psi \rangle + \langle \psi | H | \delta\psi \rangle \\ \Rightarrow \langle \psi | \psi \rangle \delta E &= \langle \delta\psi | H - E | \psi \rangle + \langle \psi | H - E | \delta\psi \rangle \end{aligned} \quad (18)$$

and hence for a non-vanishing ket $|\psi_0\rangle$ at which E is stationary

$$\langle \delta\psi | H - E | \psi_0 \rangle + \langle \psi_0 | H - E | \delta\psi \rangle = 0 \quad (19)$$

Since the variation $|\delta\psi\rangle$ was arbitrary we may replace it with $i|\delta\psi\rangle$ in (19), giving us

$$-i\langle \delta\psi | H - E | \psi_0 \rangle + i\langle \psi_0 | H - E | \delta\psi \rangle = 0 \quad (20)$$

and from (19), (20) we obtain the relations

$$\langle \delta\psi | H - E | \psi_0 \rangle = 0$$

$$\langle \psi_0 | H - E | \delta\psi \rangle = 0$$

But again since $|\psi\rangle$ is arbitrary we conclude from the above relations that

$$(H - E)|\psi_0\rangle = 0$$

$$\langle\psi_0|(H - E) = 0$$

these two relations being equivalent by virtue of the Hermiticity of H .

Thus we have that the stationary values of E are eigenvalues of H , the corresponding eigenstates being given by the inverse image under E of these stationary values.

Conversely, if E_0 is an eigenenergy of H then there exists a non-vanishing ket $|\psi_0\rangle$ such that

$$H|\psi_0\rangle = E_0|\psi_0\rangle \quad (21)$$

and comparison of (21) with (18), along with the Hermiticity of H , gives us that

$$E_0 = \frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} = E(|\psi_0\rangle)$$

is a stationary value of E .

Now, the key to the Ritz variational method is the selection of a variational subset \mathcal{V} of the state space such that the optimization of E on \mathcal{V} is tractable while the stationary values of E on \mathcal{V} approximate the stationary values of E on the entire state space to some desired degree of accuracy. Measures of the discrepancy between these two values are difficult to obtain, however, and a common approach for systems whose spectrum is bounded from below is the following:

If E_0 denotes the ground state eigenenergy of the system then from the completeness of the eigenstates of H we have that

$$\begin{aligned} E(|\psi\rangle) - E_0 &= \frac{\langle \psi | H - E_0 | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \sum_s \frac{\langle \psi | H - E_0 | s \rangle \langle s | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \sum_s (E_s - E_0) \frac{|\langle \psi | s \rangle|^2}{\langle \psi | \psi \rangle} \geq 0 \quad (|\psi\rangle \in \mathcal{E} - \{0\}) \end{aligned} \quad (22)$$

from which it follows that the smaller the stationary value of E on \mathcal{V} the better the approximation to the ground state eigenenergy.

In order to obtain an approximation to the energy E_1 of the first excited state we exclude the eigenspace \mathcal{E}_0 of the ground state eigenenergy from consideration, obtaining the result

$$\begin{aligned} E(|\psi\rangle) - E_1 &= \frac{\langle \psi | H - E_1 | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \sum_s \frac{\langle \psi | H - E_1 | s \rangle \langle s | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \sum_s (E_s - E_1) \frac{|\langle \psi | s \rangle|^2}{\langle \psi | \psi \rangle} \geq 0 \quad (|\psi\rangle \in \mathcal{E} - \mathcal{E}_0) \end{aligned} \quad (23)$$

from which it follows that the smaller the stationary value of E on $\mathcal{V} - \mathcal{E}_0$ the better the approximation to the energy of the first excited state.

Continuing in this manner we can proceed to obtain an approximation to the energy of any excited state we wish by projecting out the eigenspaces of all lower-lying eigenenergies from the state space, which is equivalent by the projection theorem to restricting E to the orthocomplement of these eigenspaces.

A considerable simplification of the problem results if the variational subset is a finite-dimensional subspace of the state space, in which case we have only to diagonalize the matrix representation of the Hamiltonian with respect to some orthonormal basis for this

variational subspace, the resulting eigenvalues giving the eigen-energies of the n lowest eigenstates, where n is the dimension of the variational subspace employed. If a set of variational parameters can be identified with the coordinates of the representation of an arbitrary element of such a subspace in some basis for that subspace then the parameters are said to be linear. Thus given a set of variational parameters their variation is effected by fixing the nonlinear parameters at various values and for each set of values of the nonlinear parameters diagonalizing the representation of the Hamiltonian in an orthonormal basis for the subspace generated by the basis with respect to which the linear parameters are the coordinates of the representation of an arbitrary element of the subspace.

Adaptation to Indefinite Operators

The arguments leading to the inequalities (20), (21) obtained above were predicated upon the existence of a lower bound for the energy spectrum of the system. We have seen, however, that the energy spectrum of a Dirac electron in the presence of a Coulomb field has no such lower bound. The spectrum of H_D^2 , on the other hand, given by $\{E_n^2 | n \in \mathbb{N}\} \cup [(mc)^2, \infty)$ (the E_n being the discrete eigenenergies of H_0), does have such a lower bound. The above obstacle can therefore be circumvented by applying the Ritz variational method to H_D^2 and from the spectrum obtained extracting the spectrum of H_0 , determining the signs of the energies lying in the continua by computing the expectation of H_0 in the corresponding eigenstate. From the spectral theorem for self-adjoint operators it follows that the bound-state eigenfunctions of H_D^2 coincide with those of H_0 .

However, as our variational subspaces will of necessity be finite-dimensional, we will in fact be finding the eigenfunctions of $P H_D^2 P$, where P is the projection from the state space onto our variational subspace, and $(P H_0 P)^2 = P H_0 P H_0 P = P H_D^2 P$. Thus the eigenfunctions computed by the above method will necessarily serve as good approximations to the bound-state eigenfunctions only in the limit of a complete variational basis, in which case P tends to the identity on the state space. However, for the lowest lying eigenstates we would expect this problem to be mild.

Calculations With A Two-Dimensional Variational Subspace

The Dirac Hamiltonian is given by

$$H_D = c \vec{\alpha} \cdot \vec{p} + mc^2 \beta + V$$

$$= c \begin{pmatrix} 0 & \vec{\sigma} \cdot \vec{p} \\ \vec{\sigma} \cdot \vec{p} & 0 \end{pmatrix} + mc^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \begin{pmatrix} V & 0 \\ 0 & V \end{pmatrix}$$

and $\begin{pmatrix} 0 & \vec{\sigma} \cdot \vec{p} \\ \vec{\sigma} \cdot \vec{p} & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2} q(r) u_{f\ell}^m \\ \frac{1}{2} r f(r) u_{f\ell}^m \end{pmatrix} = -i\hbar \vec{\sigma} \cdot \vec{p} \begin{pmatrix} 0 & \frac{\partial}{\partial r} - \frac{\kappa-1}{r} \\ \frac{\partial}{\partial r} + \frac{\kappa+1}{r} & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2} q(r) u_{f\ell}^m \\ \frac{1}{2} r f(r) u_{f\ell}^m \end{pmatrix}$

$$= i\hbar \begin{pmatrix} 0 & \frac{\partial}{\partial r} - \frac{\kappa-1}{r} \\ \frac{\partial}{\partial r} + \frac{\kappa+1}{r} & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2} q(r) u_{f\ell}^m \\ \frac{1}{2} r f(r) u_{f\ell}^m \end{pmatrix}$$

The expectation of H_D in the state $\Psi = \begin{pmatrix} \frac{1}{2} q(r) u_{f\ell}^m \\ \frac{1}{2} r f(r) u_{f\ell}^m \end{pmatrix}$

is thus given by

$$\begin{aligned} \langle \Psi | H_D | \Psi \rangle &= \hbar c \langle r^2 \left(\frac{1}{2} q \left(\frac{\kappa-1}{r} - \frac{\partial}{\partial r} \right) \frac{1}{2} r f + \frac{1}{2} f \left(\frac{\kappa+1}{r} + \frac{\partial}{\partial r} \right) \frac{1}{2} q \right) \rangle \\ &\quad + mc^2 \langle q^2 - f^2 \rangle + \langle (q^2 + f^2) V \rangle \\ &= \hbar c \left\langle \frac{2\kappa}{r} q f - q \frac{\partial f}{\partial r} + f \frac{\partial q}{\partial r} \right\rangle + mc^2 \langle q^2 - f^2 \rangle + \langle (q^2 + f^2) V \rangle \end{aligned} \quad (25)$$

Setting $\vec{f} = \langle, q$ gives us a two-dimensional variational subspace (neglecting the normalization, which has no physical consequences and, owing to the normalization independence of the functional E , has no effect upon our variational results) of the type employed by Drake and Goldman,^{7,12} and (25) becomes

$$\langle \Psi | H_D | \Psi \rangle = 2\hbar c \kappa \langle, \langle q | \frac{1}{r} | q \rangle + mc^2 (1 - \langle,^2) \langle q | q \rangle + (1 + \langle,^2) \langle q | V | q \rangle$$

and for a Hydrogenic system $V(r) = -\frac{Z\hbar c}{r}$ so that

$$\langle \Psi | H_D | \Psi \rangle = 2\hbar c \kappa \langle, \langle q | \frac{1}{r} | q \rangle + mc^2 (1 - \langle,^2) \langle q | q \rangle - Z\hbar c (1 + \langle,^2) \langle q | \frac{1}{r} | q \rangle$$

and $\langle \psi | \psi \rangle = (1 + \alpha_1^2) \langle q | q \rangle$

$$\begin{aligned} \Rightarrow E(\alpha) &\equiv \frac{\langle \psi | H_0 | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{1}{1 + \alpha_1^2} \frac{\langle \psi | H_0 | \psi \rangle}{\langle q | q \rangle} \\ &= \frac{1}{1 + \alpha_1^2} \left[mc^2(1 - \alpha_1^2) + 2\hbar c \alpha_1 \xi(\alpha_2, \dots, \alpha_n) \right] - 2\hbar c \xi(\alpha_2, \dots, \alpha_n) \end{aligned} \quad (26)$$

where $\alpha_2, \dots, \alpha_n$ are variational parameters determining the functional dependence of g upon r and

$$\xi \equiv \frac{\langle q | \frac{1}{r} | q \rangle}{\langle q | q \rangle}$$

Optimizing E with respect to $\vec{\alpha}$ gives us the equations

$$\frac{\partial E}{\partial \alpha_1} = \frac{1}{1 + \alpha_1^2} \left\{ -2mc^2\alpha_1 + 2\hbar c \alpha_1 \xi \right\} - \frac{2\alpha_1}{(1 + \alpha_1^2)^2} \left\{ mc^2(1 - \alpha_1^2) + 2\hbar c \alpha_1 \xi \right\} = 0 \quad (27)$$

$$\frac{\partial E}{\partial \alpha_j} = \frac{2\hbar c \alpha_1}{1 + \alpha_1^2} \frac{\partial \xi}{\partial \alpha_j} - 2\hbar c \xi \frac{\partial \xi}{\partial \alpha_j} = 0 \quad 2 \leq j \leq n \quad (28)$$

From (28) we have that

$$\begin{aligned} 2\hbar c \alpha_1 - 2\hbar c (1 + \alpha_1^2) &= 0 \\ \Rightarrow \alpha_1^2 - 2 \frac{\hbar c}{2\hbar c} \alpha_1 + 1 &= 0 \\ \alpha_1 &= \frac{\hbar c}{2\hbar c} \pm \left(\left(\frac{\hbar c}{2\hbar c} \right)^2 - 1 \right)^{\frac{1}{2}} = \frac{\hbar c \pm Y}{2\hbar c} \end{aligned} \quad (29)$$

while from (27) we have

$$\begin{aligned}
 (1 + \alpha_1^2) \{ \hbar c \kappa \xi - mc^2 \alpha_1 \} &= \alpha_1 \{ mc^2 (1 - \alpha_1^2) + 2 \hbar c \kappa \alpha_1 \xi \} \\
 2 mc^2 \alpha_1 &= \hbar c \kappa (1 - \alpha_1^2) \xi \\
 \Rightarrow \frac{\langle q | \gamma | q \rangle}{\langle q | q \rangle} &= \xi = \frac{2 mc \alpha_1}{\hbar \kappa (1 - \alpha_1^2)} = \frac{2 mc \frac{\kappa \pm \gamma}{2 \kappa}}{\hbar \kappa \left(1 - \left(\frac{\kappa \pm \gamma}{2 \kappa} \right)^2 \right)} \\
 &= \frac{2 mc \pm \gamma (\kappa \pm \gamma)}{\hbar \kappa \{ (2 \kappa)^2 - (\kappa^2 \pm 2 \kappa \gamma + \gamma^2 - (2 \kappa)^2) \}} \\
 &= \frac{mc \pm \gamma (\kappa \pm \gamma)}{\hbar \kappa (-\gamma^2 + \kappa)} = \frac{mc \pm \gamma}{\hbar \kappa \gamma} \quad (30)
 \end{aligned}$$

Substitution of (29) for α_1 and (30) into (26) gives

$$\begin{aligned}
 E(\pm) &= mc^2 \frac{1 - \left(\frac{\kappa \pm \gamma}{2 \kappa} \right)^2}{1 + \left(\frac{\kappa \pm \gamma}{2 \kappa} \right)^2} \\
 &= mc^2 \frac{-\gamma^2 \pm \kappa \gamma}{\kappa^2 \pm \kappa \gamma} \\
 &= \pm mc^2 \gamma / \kappa
 \end{aligned}$$

Observe that from our analytic expressions (9), (10) for the discrete

Dirac eigenenergies and eigenstates we obtain for $n' = 0$:

$$E_{0,i} = mc^2 \left(1 + \left(\frac{\pm \gamma}{\gamma} \right)^2 \right)^{-\frac{1}{2}} = mc^2 \gamma (\gamma^2 + (\pm \gamma)^2)^{-\frac{1}{2}} = mc^2 \gamma / \kappa$$

while

$$\begin{aligned}
 \frac{f(r)}{q(r)} &= \left(\frac{mc^2 - E}{mc^2 + E} \right)^{\frac{1}{2}} \\
 &= \left(\frac{1 - \left(1 + \left(\frac{\pm \gamma}{\gamma} \right)^2 \right)^{-\frac{1}{2}}}{1 + \left(1 + \left(\frac{\pm \gamma}{\gamma} \right)^2 \right)^{-\frac{1}{2}}} \right)^{\frac{1}{2}} \\
 &= \left(\frac{1 - \gamma / \kappa}{1 + \gamma / \kappa} \right)^{\frac{1}{2}} \times \left(\frac{1 - \gamma / \kappa}{1 - \gamma / \kappa} \right)^{\frac{1}{2}} \frac{|\kappa|}{|\kappa|} \\
 &= \frac{|\kappa| - \gamma}{(\kappa^2 - \gamma^2)^{\frac{1}{2}}} = \frac{|\kappa| - \gamma}{2 \kappa}
 \end{aligned}$$

and

$$\frac{\langle q | \gamma | q \rangle}{\langle q | q \rangle} = \frac{\int_0^\infty r^{2\gamma-1} e^{-2\lambda r} dr}{\int_0^\infty r^{2\gamma} e^{-2\lambda r} dr} = \lambda / \gamma = \frac{mc \pm \gamma}{\hbar |\kappa| \gamma}$$

Thus we see that exact values for the eigenenergy and linear variational parameter are obtained upon optimizing the expectation

of the Dirac Hamiltonian in the state $g(r) \begin{pmatrix} \frac{1}{r} u_{f1}^m \\ i_r u_{f2}^m \end{pmatrix}$ of

our two-dimensional variational subspace, but the eigenstate is determined only up to a radial factor $q(r)$ such that

$$\frac{\langle q | \hat{H} | q \rangle}{\langle q | q \rangle} = \frac{mc^2 \beta}{\hbar \kappa \gamma}$$

In addition the eigenenergy obtained in the above analysis is insensitive to the sign of κ , resulting in the generation of energies lying below the ground state eigenenergy, corresponding to the $n' = 0$ state which is disallowed for $\kappa > 0$.

Repeating the above analysis with H_D^2 in place of H_D , we have upon squaring (4)

$$\begin{aligned} H_D^2 &= (c \vec{\alpha} \cdot \vec{p} + mc^2 \beta + V)(c \vec{\alpha} \cdot \vec{p} + mc^2 \beta + V) \\ &= c^2 p^2 + (mc^2)^2 + V^2 + mc^2 \{ \vec{\alpha}, \beta \} + 2mc^2 V \beta + c \{ \vec{\alpha}, \vec{p}, V \} \\ &= c^2 \left(-\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2}{r^2} \right) + (mc^2)^2 + V^2 + 2mc^2 V \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + c \{ \vec{\alpha}, \vec{p}, V \} \\ \text{and } \{ \vec{\alpha}, \vec{p}, V \} \begin{pmatrix} \frac{1}{r} q(r) u_{f1}^m \\ i_r f(r) u_{f2}^m \end{pmatrix} &= \begin{pmatrix} 0 & \vec{\sigma} \cdot \vec{p} V + V \vec{\sigma} \cdot \vec{p} \\ \vec{\sigma} \cdot \vec{p} V + V \vec{\sigma} \cdot \vec{p} & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{r} q(r) u_{f1}^m \\ i_r f(r) u_{f2}^m \end{pmatrix} \\ &= i \vec{\sigma} \cdot \hat{r} \begin{pmatrix} 0 & (-\hbar \frac{\partial^2}{\partial r^2} + \frac{1}{2} \vec{\sigma} \cdot \vec{L}) V + V (-\hbar \frac{\partial^2}{\partial r^2} + \frac{1}{2} \vec{\sigma} \cdot \vec{L}) \\ (-\hbar \frac{\partial^2}{\partial r^2} + \frac{1}{2} \vec{\sigma} \cdot \vec{L}) V + V (-\hbar \frac{\partial^2}{\partial r^2} + \frac{1}{2} \vec{\sigma} \cdot \vec{L}) & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{r} q(r) u_{f1}^m \\ i_r f(r) u_{f2}^m \end{pmatrix} \\ &= -2i \vec{\sigma} \cdot \hat{r} \begin{pmatrix} 0 & \hbar V \frac{\partial}{\partial r} + \frac{1}{2} \hbar \frac{\partial V}{\partial r} - \frac{1}{r} \vec{\sigma} \cdot \vec{L} \\ \hbar V \frac{\partial}{\partial r} + \frac{1}{2} \hbar \frac{\partial V}{\partial r} - \frac{1}{r} V \vec{\sigma} \cdot \vec{L} & 0 \end{pmatrix} \\ &= -2i \hbar \vec{\sigma} \cdot \hat{r} \begin{pmatrix} 0 & V \frac{\partial}{\partial r} + \frac{1}{2} \frac{\partial V}{\partial r} - \frac{\kappa-1}{r} V \\ V \frac{\partial}{\partial r} + \frac{1}{2} \frac{\partial V}{\partial r} + \frac{\kappa+1}{r} V & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{r} q(r) u_{f1}^m \\ i_r f(r) u_{f2}^m \end{pmatrix} \end{aligned}$$

The expectation of H_0^2 in the state $\psi = \begin{pmatrix} \chi q(r) u_{l+1}^{\chi} \\ i/r f(r) u_{l+1}^{\chi} \end{pmatrix}$ is then given by

$$\begin{aligned} \langle \psi | H_0^2 | \psi \rangle &= (\hbar c)^2 \langle -(q \frac{\partial^2}{\partial r^2} + f \frac{\partial^2}{\partial r^2}) + l(l+1)q^2 + l(l+1)f^2 \rangle + (mc^2)^2 \langle q^2 + f^2 \rangle + 2mc^2 \langle (q^2 - f^2) V \rangle \\ &\quad - 2\hbar c \langle r \frac{\partial}{\partial r} (V \frac{\partial}{\partial r} + \frac{1}{2} \frac{\partial V}{\partial r} - \frac{\kappa-1}{r} V) \frac{\partial}{\partial r} - f (V \frac{\partial}{\partial r} + \frac{1}{2} \frac{\partial V}{\partial r} + \frac{\kappa+1}{r} V) \frac{\partial}{\partial r} \rangle + \langle (q^2 + f^2) V^2 \rangle \\ &= (\hbar c)^2 \langle \kappa(\kappa+1) \frac{q^2}{r^2} + \kappa(\kappa-1) \frac{f^2}{r^2} - (q \frac{\partial^2 q}{\partial r^2} + f \frac{\partial^2 f}{\partial r^2}) \rangle + (mc^2)^2 \langle q^2 + f^2 \rangle + 2mc^2 \langle (q^2 - f^2) V \rangle \\ &\quad - 2\hbar c \langle -2\kappa q f \frac{V}{r} + V (q \frac{\partial f}{\partial r} - f \frac{\partial q}{\partial r}) \rangle + \langle (q^2 + f^2) V^2 \rangle \end{aligned}$$

Again setting $f = \alpha_1 q$ we obtain

$$\begin{aligned} \langle \psi | H_0^2 | \psi \rangle &= (\hbar c)^2 \{ [\kappa^2(1+\alpha_1^2) + \kappa(1-\alpha_1^2)] \langle q | \frac{1}{r^2} | q \rangle - (1+\alpha_1^2) \langle q | \frac{\partial^2}{\partial r^2} | q \rangle \\ &\quad + (mc^2)^2 (1+\alpha_1^2) \langle q | q \rangle + 2mc^2 (1-\alpha_1^2) \langle q | V | q \rangle + 4\hbar \kappa c \alpha_1 \langle q | \frac{V}{r} | q \rangle \\ &\quad + (1+\alpha_1^2) \langle q | V^2 | q \rangle \} \end{aligned}$$

and for a hydrogenic system $V(r) = -\frac{Z\alpha\hbar c}{r}$, giving us

$$\begin{aligned} \langle \psi | H_0^2 | \psi \rangle &= (\hbar c)^2 \{ \kappa^2(1+\alpha_1^2) + \kappa(1-\alpha_1^2) \} \langle q | \frac{1}{r^2} | q \rangle - (\hbar c)^2 (1+\alpha_1^2) \langle q | \frac{\partial^2}{\partial r^2} | q \rangle \\ &\quad + (mc^2)^2 (1+\alpha_1^2) \langle q | q \rangle - 2mc^2 Z \alpha \hbar c (1-\alpha_1^2) \langle q | \frac{1}{r} | q \rangle - 4\kappa Z \alpha \hbar c^2 \alpha_1 \langle q | \frac{1}{r^2} | q \rangle \\ &\quad + (Z\alpha\hbar c)^2 (1+\alpha_1^2) \langle q | \frac{1}{r^2} | q \rangle \} \end{aligned}$$

and again

$$\begin{aligned} \langle \psi | \psi \rangle &= (1+\alpha_1^2) \langle q | q \rangle \\ \Rightarrow \tilde{E}(Z) &= \frac{\langle \psi | H_0^2 | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= (mc^2)^2 - (\hbar c)^2 \frac{\langle q | \frac{\partial^2}{\partial r^2} | q \rangle}{\langle q | q \rangle} - 2mc^2 Z \alpha \hbar c \frac{1-\alpha_1^2}{1+\alpha_1^2} \frac{\langle q | \frac{1}{r} | q \rangle}{\langle q | q \rangle} \\ &\quad + (\hbar c)^2 \{ (Z\alpha)^2 + \kappa^2 + \kappa \frac{1-\alpha_1^2}{1+\alpha_1^2} - 4\kappa Z \alpha \frac{\alpha_1}{1+\alpha_1^2} \} \frac{\langle q | \frac{1}{r^2} | q \rangle}{\langle q | q \rangle} \quad (32) \end{aligned}$$

Optimizing \tilde{E} with respect to α_1 , we get

$$\frac{\partial \tilde{E}}{\partial \alpha_1} = 8mc^2 \tilde{z} \kappa \frac{\alpha_1}{(1+\alpha_1^2)^2} \frac{\langle q | \frac{1}{r} | q \rangle}{\langle q | q \rangle} - 4(\hbar c)^2 \kappa \left\{ \frac{\alpha_1}{(1+\alpha_1^2)^2} + \tilde{z} \alpha_1 \frac{1-\alpha_1^2}{(1+\alpha_1^2)^2} \right\} \frac{\langle q | \frac{1}{r^2} | q \rangle}{\langle q | q \rangle} = 0$$

$$\Rightarrow 2mc^2 \tilde{z} \kappa \alpha_1 \langle q | \frac{1}{r} | q \rangle = (\hbar c)^2 \kappa \left\{ \alpha_1 + \tilde{z} \alpha_1 (1-\alpha_1^2) \right\} \langle q | \frac{1}{r^2} | q \rangle$$

$$\frac{2mc^2 \tilde{z} \kappa}{\hbar c \kappa} \alpha_1 \frac{\langle q | \frac{1}{r} | q \rangle}{\langle q | \frac{1}{r^2} | q \rangle} = \alpha_1 + \tilde{z} \alpha_1 (1-\alpha_1^2)$$

$$\tilde{z} \alpha_1 \frac{1-\alpha_1^2}{\alpha_1} = \frac{2mc^2 \tilde{z} \kappa}{\hbar c \kappa} \frac{\langle q | \frac{1}{r} | q \rangle}{\langle q | \frac{1}{r^2} | q \rangle} - 1$$

$$= \frac{2mc^2 \tilde{z} \kappa}{\hbar c \kappa} \rho - 1, \quad \rho \equiv \frac{\langle q | \frac{1}{r} | q \rangle}{\langle q | \frac{1}{r^2} | q \rangle} \quad (33)$$

$$= 2A, \quad A \equiv \frac{mc^2 \tilde{z} \kappa}{\hbar c \kappa} \rho - \frac{1}{2} \quad (34)$$

$$\Rightarrow \alpha_1^2 + 2 \frac{A}{\tilde{z} \kappa} \alpha_1 - 1 = 0$$

$$\begin{aligned} \alpha_1 &= -\frac{A}{\tilde{z} \kappa} \pm \left(\left(\frac{A}{\tilde{z} \kappa} \right)^2 + 1 \right)^{\frac{1}{2}} \\ &= -\frac{A}{\tilde{z} \kappa} \left\{ 1 - \left(1 + \left(\frac{\tilde{z} \kappa}{A} \right)^2 \right)^{\frac{1}{2}} \right\} \\ &= -\frac{A}{\tilde{z} \kappa} (1-R) \end{aligned}$$

where $R \equiv \left(1 + \left(\frac{\tilde{z} \kappa}{A} \right)^2 \right)^{\frac{1}{2}}$

Thus $\frac{1-\alpha_1^2}{1+\alpha_1^2} = \frac{1 - \left(\frac{A}{\tilde{z} \kappa} \right)^2 (1-R)^2}{1 + \left(\frac{A}{\tilde{z} \kappa} \right)^2 (1-R)^2}$

$$\begin{aligned} &= \frac{\left(\frac{\tilde{z} \kappa}{A} \right)^2 - \left\{ 1 - 2R + 1 + \left(\frac{\tilde{z} \kappa}{A} \right)^2 \right\}}{\left(\frac{\tilde{z} \kappa}{A} \right)^2 + 1 - 2R + \left(\frac{\tilde{z} \kappa}{A} \right)^2} \\ &= \frac{R-1}{R^2-R} \\ &= \frac{1}{R} \end{aligned}$$

(35)

$$\begin{aligned}
 \text{and } \frac{2\alpha_1}{1+\alpha_1^2} &= \frac{2\alpha_1}{1-\alpha_1^2} \frac{1-\alpha_1^2}{1+\alpha_1^2} \\
 &= \frac{2\alpha_1}{1-\alpha_1^2} \frac{1}{R} \\
 &= \frac{2\alpha_1}{AR}
 \end{aligned} \tag{36}$$

while from (34)

$$\langle q | \frac{1}{r} | q \rangle = \frac{\hbar \kappa}{mc \Xi \alpha_1} (A + \frac{1}{2}) \langle q | \frac{1}{r^2} | q \rangle \tag{37}$$

Substitution of (35), (36) and (37) into (32) gives us

$$\begin{aligned}
 \hat{E}(2) &= (mc^2)^2 - (\hbar c)^2 \frac{\langle q | \frac{\partial^2}{\partial r^2} | q \rangle}{\langle q | q \rangle} + \left\{ -2mc^2 \Xi \hbar c \frac{\hbar \kappa}{mc \Xi \alpha_1} \frac{A + \frac{1}{2}}{R} + (\hbar c)^2 \left[(\Xi \alpha_1)^2 + \kappa^2 + \frac{\kappa}{R} - 2\kappa \frac{(\Xi \alpha_1)^2}{AR} \right] \right. \\
 &\quad \left. \times \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle} \right\} \\
 &= (mc^2)^2 - (\hbar c)^2 \frac{\langle q | \frac{\partial^2}{\partial r^2} | q \rangle}{\langle q | q \rangle} + (\hbar c)^2 \left\{ (\Xi \alpha_1)^2 + \kappa^2 - \frac{2\kappa A}{R} \left[1 + \left(\frac{\Xi \alpha_1}{A} \right)^2 \right] \right\} \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle} \\
 &= (mc^2)^2 - (\hbar c)^2 \frac{\langle q | \frac{\partial^2}{\partial r^2} | q \rangle}{\langle q | q \rangle} + (\hbar c)^2 \left\{ (\Xi \alpha_1)^2 + \kappa^2 - 2\kappa AR \right\} \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle}
 \end{aligned}$$

Introducing nonlinear parameters α_2, α_3 such that

$$\begin{aligned}
 q(r) &= r^{\alpha_2} e^{-\alpha_3 r} \\
 \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle} &= \frac{\int_0^\infty r^{2\alpha_2-2} e^{-2\alpha_3 r} dr}{\int_0^\infty r^{2\alpha_2} e^{-2\alpha_3 r} dr} \\
 &= \frac{(2\alpha_3)^2}{2\alpha_2(2\alpha_2-1)} = \frac{2\alpha_3^2}{\alpha_2(2\alpha_2-1)}
 \end{aligned} \tag{38}$$

$$\begin{aligned}
 \frac{\langle q | r^3 | q \rangle}{\langle q | q \rangle} &= \frac{\int_0^\infty r^{2\alpha_2+1} e^{-2\alpha_3 r} dr}{\int_0^\infty r^{2\alpha_2} e^{-2\alpha_3 r} dr} \\
 &= \frac{2\alpha_3}{2\alpha_2} = \frac{\alpha_3}{\alpha_2}
 \end{aligned} \tag{39}$$

$$\begin{aligned}
\frac{\langle q | \frac{\partial^2}{\partial r^2} | q \rangle}{\langle q | q \rangle} &= \frac{\int_0^\infty \left[\alpha_2(\alpha_2-1)r^{2\alpha_2-2} - 2\alpha_2\alpha_3 r^{2\alpha_2-1} + \alpha_3^2 r^{2\alpha_2} \right] e^{-2\alpha_3 r} dr}{\int_0^\infty r^{2\alpha_2} e^{-2\alpha_3 r} dr} \\
&= \alpha_2(\alpha_2-1) \frac{(2\alpha_3)^2}{2\alpha_2(2\alpha_2-1)} - 2\alpha_2\alpha_3 \frac{2\alpha_3}{2\alpha_2} + \alpha_3^2 \\
&= \frac{2\alpha_3^2}{\alpha_2(2\alpha_2-1)} \left[\alpha_2(\alpha_2-1) - \alpha_2(2\alpha_2-1) + \frac{1}{2}\alpha_2(2\alpha_2-1) \right] \\
&= -\frac{1}{2} \alpha_2 \langle q | r^{-2} | q \rangle
\end{aligned}$$

(40)

From (38) and (39) we have that

$$\begin{aligned}
\rho &\equiv \frac{\langle q | r^{-1} | q \rangle}{\langle q | r^{-2} | q \rangle} \\
&= \frac{2\alpha_2-1}{2\alpha_3}
\end{aligned}$$

$$\Rightarrow \rho^2 \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle} = \frac{2\alpha_2-1}{\alpha_2}$$

$$1 - \rho^2 \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle} = \frac{1}{2\alpha_2}$$

$$\alpha_2 = \frac{\frac{1}{2}}{1 - \rho^2 \frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle}}$$

(41)

Thus denoting $\frac{\langle q | r^{-2} | q \rangle}{\langle q | q \rangle}$ by σ we have from (40) and (41) that

$$\frac{\langle q | \frac{\partial^2}{\partial r^2} | q \rangle}{\langle q | q \rangle} = \frac{-\frac{1}{2} \sigma}{1 - \sigma \rho^2}$$

and

$$\tilde{E}(\alpha) = (mc)^2 + (\hbar c)^2 \left\{ \frac{\frac{1}{2}}{1-\sigma\rho^2} + (\alpha-1)^2 + \kappa^2 - 2\kappa AR \right\} \sigma$$

Now, since

$$\begin{aligned} \left| \frac{\partial(\rho, \sigma)}{\partial(\alpha_2, \alpha_3)} \right| &= \begin{vmatrix} \frac{1}{2} & -\frac{2\alpha_2-1}{2\alpha_2^2} \\ -(4\alpha_2-1)\frac{2\alpha_2^2}{\alpha_2^2(2\alpha_2-1)^2} & -\frac{4\alpha_2}{\alpha_2(2\alpha_2-1)} \end{vmatrix} \\ &= \frac{4}{\alpha_2(2\alpha_2-1)} - \frac{4\alpha_2-1}{\alpha_2^2(2\alpha_2-1)} \\ &= \frac{1}{\alpha_2^2(2\alpha_2-1)} \neq 0 \quad (\forall \alpha_2 \in \mathbb{R} - \{\frac{1}{2}\}) \end{aligned}$$

we can treat ρ and σ as the independent variables and optimize \tilde{E} with respect to them, giving

$$\begin{aligned} \frac{\partial \tilde{E}}{\partial \rho} &= (\hbar c)^2 \sigma \left\{ \frac{\frac{1}{2} \sigma \rho}{(1-\sigma\rho^2)^2} - 2\kappa \frac{\partial A}{\partial \rho} (R + A \frac{\partial R}{\partial A}) \right\} \\ &= (\hbar c)^2 \sigma \left\{ \frac{\frac{1}{2} \sigma \rho}{(1-\sigma\rho^2)^2} - \frac{2mc^2 \kappa}{\hbar} (R - (\frac{\kappa}{A})^2 R^{-1}) \right\} \\ &= (\hbar c)^2 \sigma \left\{ \frac{\frac{1}{2} \sigma \rho}{(1-\sigma\rho^2)^2} - \frac{2mc^2 \kappa}{\hbar} R^{-1} \right\} \\ &= 0 \end{aligned}$$

$$\begin{aligned} \frac{\partial \tilde{E}}{\partial \sigma} &= (\hbar c)^2 \left\{ \frac{\frac{1}{2}}{1-\sigma\rho^2} + (\alpha-1)^2 + \kappa^2 - 2\kappa AR + \frac{\frac{1}{2} \rho^2 \sigma}{(1-\sigma\rho^2)^2} \right\} \\ &= 0 \end{aligned}$$

From the first of the above equations we obtain

$$\begin{aligned} \frac{1}{4} \rho \sigma R &= \frac{m c^2 \epsilon}{\hbar} (1 - \sigma \rho^2)^2 \\ &= \frac{m c^2 \epsilon}{\hbar} \frac{1}{4 \alpha_2^2} \end{aligned}$$

or, since $\rho \sigma = \frac{1}{2} \rho^2 \sigma$

$$= \frac{1}{2} \rho \left(1 - \frac{1}{2 \alpha_2}\right)$$

$$\frac{R}{4 \rho} \left(1 - \frac{1}{2 \alpha_2}\right) = \frac{m c^2 \epsilon}{\hbar} \frac{1}{4 \alpha_2^2}$$

$$\frac{1}{\alpha_2^2} + \frac{1}{2} \frac{\hbar}{m c^2 \epsilon} \frac{R}{\rho} \frac{1}{\alpha_2} - \frac{\hbar}{m c^2 \epsilon} \frac{R}{\rho} = 0$$

$$\frac{1}{\alpha_2} = -\frac{1}{4} \frac{\hbar}{m c^2 \epsilon} \frac{R}{\rho} + \frac{1}{4} \left(\left(\frac{\hbar}{m c^2 \epsilon} \frac{R}{\rho} \right)^2 + \frac{16 \hbar}{m c^2 \epsilon} \frac{R}{\rho} \right)^{\frac{1}{2}}$$

$$\alpha_2 = 4 \rho \left\{ \frac{-\hbar}{m c^2 \epsilon} R + \left(\left(\frac{\hbar}{m c^2 \epsilon} \frac{R}{\rho} \right)^2 + \frac{16 \hbar}{m c^2 \epsilon} R \rho \right)^{\frac{1}{2}} \right\}^{-1}$$

(42)

while from the second equation we have

$$\begin{aligned} 2 \kappa A R - (Z \epsilon)^2 - \kappa^2 &= \frac{\frac{1}{4}}{(1 - \sigma \rho^2)^2} \\ &= \alpha_2^2 \end{aligned} \quad (43)$$

Squaring (42), comparing the result with (43), and substituting (34) for

ρ gives us the nonlinear equation

$$\begin{aligned} 2 \kappa A R - (Z \epsilon)^2 - \kappa^2 &= \left(\frac{2 \hbar \kappa}{m c^2 \epsilon} (2A+1) \left\{ \frac{-\hbar}{m c^2 \epsilon} R + \left(\left(\frac{\hbar}{m c^2 \epsilon} R \right)^2 + 8 \kappa \left(\frac{\hbar}{m c^2 \epsilon} \right)^2 (2A+1) R \right)^{\frac{1}{2}} \right\}^{-1} \right)^2 \\ &= 4 \kappa^2 (2A+1)^2 \left\{ (R^2 + 8 \kappa (2A+1) R)^{\frac{1}{2}} - R \right\}^{-2} \end{aligned}$$

(44)

in A. If $\kappa < 0$ and we take $A = -\gamma$ then $AR = -\gamma \left(1 + \left(\frac{\vec{z}\kappa}{\gamma}\right)^2\right)^{1/2} = \kappa$
and

$$\begin{aligned} (R^2 + 8R\kappa(2A+1))^{1/2} - R &= \left(\frac{\kappa^2}{A^2} + 8\frac{\kappa^2}{A}(2A+1)\right)^{1/2} - \kappa/A \\ &= \kappa/A \left\{ (1 + 8A(2A+1))^{1/2} - 1 \right\} \\ &= \kappa/A \left\{ -(4A+1) - 1 \right\} \\ &= -\frac{2\kappa}{A}(2A+1) \end{aligned}$$

and thus $A = -\gamma$ gives a solution of (44) for $\kappa < 0$.

$A = -\gamma \Rightarrow R = -\kappa/\gamma$ and from (43) we have that

$$\begin{aligned} 1 - \sigma\rho^2 &= \frac{1}{2} (2\kappa AR - (\vec{z}\kappa)^2 - \kappa^2)^{-1/2} = \frac{1}{2} \gamma^{-1} \\ \sigma\rho^2 &= 1 - \frac{1}{2} \gamma^{-1} \end{aligned}$$

while from (34) $\rho = \frac{\hbar\kappa}{mc\vec{z}\kappa} \left(\frac{1}{2} - \gamma\right)$

Thus

$$\sigma = \left(\frac{mc\vec{z}\kappa}{\hbar\kappa}\right)^2 \frac{1 - \frac{1}{2}\gamma^{-1}}{\left(\frac{1}{2} - \gamma\right)^2} = -\left(\frac{mc\vec{z}\kappa}{\hbar\kappa}\right)^2 \gamma^{-1} \left(\frac{1}{2} - \gamma\right)^{-1}$$

and finally we have that

$$\begin{aligned} \hat{E}(\vec{z}) &= (mc^2)^2 - (\hbar c)^2 \left\{ \frac{\hbar^2}{2\gamma^{-1}} + (\vec{z}\kappa)^2 + \kappa^2 - 2\kappa^2 \left(\frac{mc\vec{z}\kappa}{\hbar\kappa}\right)^2 \gamma^{-1} \left(\frac{1}{2} - \gamma\right)^{-1} \right\} \\ &= (mc^2)^2 \left\{ 1 - \left(\frac{\vec{z}\kappa}{\kappa}\right)^2 \left(\frac{1}{2}\gamma - \gamma^2\right) \gamma^{-1} \left(\frac{1}{2} - \gamma\right)^{-1} \right\} \\ &= (mc^2)^2 \left(1 - \left(\frac{\vec{z}\kappa}{\kappa}\right)^2\right) \\ &= \left(\frac{\gamma}{\kappa}\right)^2 (mc^2)^2 \end{aligned}$$

For $K > 0$ we obtain the numerical solutions given in Table 1.

Thus optimization of the functional E gives us exact results for the eigenenergies and eigenfunctions for non-degenerate negative K states and for $K > 0$ states the variational approximations to the eigenenergies lie above the actual values.

Calculations With Multi-Dimensional Variational Subspaces

The Generalized Slater-type Orbital (STO) Basis

Introducing the functions $v_{i\ell m}^p, w_{i\ell m}^q$ defined by

$$v_{i\ell m}^p = \frac{1}{r} \xi^p(r) \begin{pmatrix} u_{i\ell}^m \\ 0 \end{pmatrix}$$

$$w_{i\ell m}^q = \frac{1}{r} \xi^q(r) \begin{pmatrix} 0 \\ i u_{i\ell}^m \end{pmatrix}$$

with $\xi^p(r) = r^{\gamma+p} e^{-\lambda r}$, γ and λ being non-linear parameters, observe that

$$\langle v_{i\ell m}^p | v_{i'\ell' m'}^{p'} \rangle = \langle w_{i\ell m}^p | w_{i'\ell' m'}^{p'} \rangle = N_{pp'} \delta_{ii'} \delta_{\ell\ell'} \delta_{mm'}$$

$$\langle v_{i\ell m}^p | w_{i'\ell' m'}^{p'} \rangle = \langle w_{i\ell m}^p | v_{i'\ell' m'}^{p'} \rangle = 0$$

$$\text{where } N_{pp'} \equiv \frac{\Gamma(2\gamma + p + p' + 1)}{(2\lambda)^{2\gamma + p + p' + 1}}$$

Introducing ω defined by

$$\omega_{pp'} = \frac{N_{pp'}}{(N_{pp} N_{p'p'})^{1/2}}$$

we obtain the normalized functions

$$\hat{v}_{i\ell m}^p = N_{pp}^{-1/2} v_{i\ell m}^p$$

$$\hat{w}_{i\ell m}^q = N_{qq}^{-1/2} w_{i\ell m}^q$$

The generalized ST0 basis is given by

$$\beta = \{ \hat{v}_{ilm}^p, \hat{w}_{ilm}^q / 0 \leq p \leq N, 0 \leq q \leq M; m, N \in \mathbb{N}_0 \}$$

for fixed angular momentum quantum numbers j, l, m .

Observe that

$$\langle \hat{v}_{ilm}^p | \hat{v}_{ilm}^{p'} \rangle = \langle \hat{w}_{ilm}^q | \hat{w}_{ilm}^{q'} \rangle = \delta_{pp'} \delta_{ll'} \delta_{mm'} \omega_{pp'}$$

and introducing $n \equiv |p - p'|$

$$\sigma \equiv \gamma + \max\{p, p'\}$$

we have for $p \geq p'$

$$\omega_{pp'} = \frac{N_{pp'}}{(N_{pp} N_{p'p'})^{1/2}}$$

$$= \frac{\Gamma(2\gamma + p + p' + 1)}{(\Gamma(2\gamma + 2p + 1) \Gamma(2\gamma + 2p' + 1))^{1/2}}$$

$$= \frac{(2\gamma + p + p')(2\gamma + p + p' - 1) \cdots (2\gamma + 2p' + 1)}{((2\gamma + 2p)(2\gamma + 2p - 1) \cdots (2\gamma + 2p' + 1))^{1/2}}$$

$$= \frac{(2\sigma - n)(2\sigma - n - 1) \cdots (2\sigma - 2n + 1)}{(2\sigma(2\sigma - 1) \cdots (2\sigma - 2n + 1))^{1/2}}$$

$$= \frac{(2\sigma - n)(2\sigma - n - 1) \cdots (2\sigma - 2n + 1)}{(2\sigma(2\sigma - 1) \cdots (2\sigma - n + 1)(2\sigma - n)(2\sigma - n - 1) \cdots (2\sigma - 2n + 1))^{1/2}}$$

$$= \left(\frac{(2\sigma - n)(2\sigma - n - 1) \cdots (2\sigma - 2n + 1)}{2\sigma(2\sigma - 1) \cdots (2\sigma - n + 1)} \right)^{1/2}$$

and similarly for $p < p'$.

Hence

$$\begin{aligned}
 (\forall p, p' \in \mathcal{N}_0) \omega_{pp'} &= \left(\prod_{i=0}^{n-1} \frac{2\sigma - n - i}{2\sigma - i} \right)^{\frac{1}{2}} \\
 &= \left(\prod_{i=0}^{n-1} \left\{ 1 - \frac{n}{2\sigma - i} \right\} \right)^{\frac{1}{2}}
 \end{aligned}$$

Matrix Elements of the Hamiltonian

From (24) we have for the matrix elements of the Dirac Hamiltonian in the STO basis:

$$\begin{aligned} \langle \hat{u}_{\ell m}^{\rho} | H_0 | \hat{u}_{\ell' m'}^{\rho'} \rangle &= \left\langle \frac{1}{r} \xi^{\rho} \begin{pmatrix} u_{\ell \ell}^m \\ 0 \end{pmatrix} \middle| H_0 \middle| \frac{1}{r} \xi^{\rho'} \begin{pmatrix} u_{\ell' \ell'}^{m'} \\ 0 \end{pmatrix} \right\rangle \\ &= \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} \int_0^{\infty} \{ m c^2 + V(r) \} \xi^{\rho}(r) \xi^{\rho'}(r) dr \\ &= \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} N_{\rho \rho}^{-\frac{1}{2}} N_{\rho' \rho'}^{-\frac{1}{2}} \int_0^{\infty} \{ m c^2 + V(r) \} r^{2\gamma + \rho + \rho'} e^{-2\lambda r} dr \end{aligned}$$

$$\begin{aligned} \langle \hat{w}_{\ell m}^{\rho} | H_0 | \hat{u}_{\ell' m'}^{\rho'} \rangle &= \left\langle \frac{1}{r} \xi^{\rho} \begin{pmatrix} 0 \\ i u_{\ell \ell}^m \end{pmatrix} \middle| H_0 \middle| \frac{1}{r} \xi^{\rho'} \begin{pmatrix} u_{\ell' \ell'}^{m'} \\ 0 \end{pmatrix} \right\rangle \\ &= \hbar c \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} N_{\rho \rho}^{-\frac{1}{2}} N_{\rho' \rho'}^{-\frac{1}{2}} \int_0^{\infty} r \xi^{\rho}(r) \left(\frac{\partial}{\partial r} + \frac{\kappa+1}{r} \right) \frac{1}{r} \xi^{\rho'}(r) dr \\ &= \hbar c \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} N_{\rho \rho}^{-\frac{1}{2}} N_{\rho' \rho'}^{-\frac{1}{2}} \int_0^{\infty} r \xi^{\rho}(r) \left(-\frac{1}{r^2} \xi^{\rho'}(r) + \frac{1}{r} \frac{d\xi^{\rho'}}{dr} + \frac{\kappa+1}{r^2} \xi^{\rho'}(r) \right) dr \\ &= \hbar c \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} N_{\rho \rho}^{-\frac{1}{2}} N_{\rho' \rho'}^{-\frac{1}{2}} \int_0^{\infty} \{ (\kappa + \gamma + \rho') r^{2\gamma + \rho + \rho' - 1} - \lambda r^{2\gamma + \rho + \rho'} \} e^{-2\lambda r} dr \\ &= \hbar c \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} N_{\rho \rho}^{-\frac{1}{2}} N_{\rho' \rho'}^{-\frac{1}{2}} \left\{ (\kappa + \gamma + \rho') \frac{\Gamma(2\gamma + \rho + \rho')}{(2\lambda)^{2\gamma + \rho + \rho'}} - \lambda \frac{\Gamma(2\gamma + \rho + \rho' + 1)}{(2\lambda)^{2\gamma + \rho + \rho' + 1}} \right\} \\ &= \hbar c \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} \left\{ \frac{2\lambda(\kappa + \gamma + \rho')}{2\gamma + \rho + \rho'} - \lambda \right\} \omega_{\rho \rho'} \\ &= \hbar c \lambda \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} \frac{2\kappa + \rho' - \rho}{2\gamma + \rho' + \rho} \omega_{\rho \rho'} \\ &= \langle \hat{u}_{\ell' m'}^{\rho'} | H_0 | \hat{w}_{\ell m}^{\rho} \rangle \end{aligned}$$

$$\begin{aligned} \langle \hat{w}_{\ell m}^{\rho} | H_0 | \hat{w}_{\ell' m'}^{\rho'} \rangle &= \left\langle \frac{1}{r} \xi^{\rho}(r) \begin{pmatrix} 0 \\ i u_{\ell \ell}^m \end{pmatrix} \middle| H_0 \middle| \frac{1}{r} \xi^{\rho'}(r) \begin{pmatrix} 0 \\ i u_{\ell' \ell'}^{m'} \end{pmatrix} \right\rangle \\ &= \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} \int_0^{\infty} \{ -m c^2 + V(r) \} \xi^{\rho}(r) \xi^{\rho'}(r) dr \\ &= \delta_{jj'} \delta_{\ell \ell'} \delta_{mm'} N_{\rho \rho}^{-\frac{1}{2}} N_{\rho' \rho'}^{-\frac{1}{2}} \int_0^{\infty} \{ -m c^2 + V(r) \} r^{2\gamma + \rho + \rho'} e^{-2\lambda r} dr \end{aligned}$$

For a hydrogenic system $V(r) = -\frac{Ze^2}{r}$ and the matrix elements of the Hamiltonian are thus given by

$$\begin{aligned} \langle \hat{\psi}_{l'm}^{\rho} | H_0 | \hat{\psi}_{l'm'}^{\rho'} \rangle &= \delta_{jj'} \delta_{ll'} \delta_{mm'} N_{\rho\rho'}^{-\frac{1}{2}} N_{\rho'\rho'}^{-\frac{1}{2}} \int_0^{\infty} \{ mc^2 r^{2\gamma+\rho+\rho'} - Ze^2 r^{2\gamma+\rho+\rho'-1} \} e^{-2\lambda r} dr \\ &= \delta_{jj'} \delta_{ll'} \delta_{mm'} N_{\rho\rho'}^{-\frac{1}{2}} N_{\rho'\rho'}^{-\frac{1}{2}} \left\{ mc^2 \frac{\Gamma(2\gamma+\rho+\rho'+1)}{(2\lambda)^{2\gamma+\rho+\rho'+1}} - Ze^2 \frac{\Gamma(2\gamma+\rho+\rho')}{(2\lambda)^{2\gamma+\rho+\rho'}} \right\} \\ &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ mc^2 - \frac{2\lambda Ze^2}{2\gamma+\rho+\rho'} \right\} \omega_{\rho\rho'} \end{aligned}$$

$$\begin{aligned} \langle \hat{\psi}_{l'm}^{\rho} | H_0 | \hat{\psi}_{l'm'}^{\rho'} \rangle &= \hbar c \lambda \delta_{jj'} \delta_{ll'} \delta_{mm'} \frac{2\gamma+\rho'-\rho}{2\gamma+\rho'+\rho} \omega_{\rho\rho'} \\ &= \langle \hat{\psi}_{l'm'}^{\rho'} | H_0 | \hat{\psi}_{l'm}^{\rho} \rangle \end{aligned}$$

$$\langle \hat{\psi}_{l'm}^{\rho} | H_0 | \hat{\psi}_{l'm'}^{\rho'} \rangle = -\delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ mc^2 + \frac{2\lambda Ze^2}{2\gamma+\rho+\rho'} \right\} \omega_{\rho\rho'}$$

Matrix Elements of the Squared Hamiltonian

From (25) we have for the matrix elements of the squared Hamiltonian in the unnormalized STO basis:

$$\begin{aligned}
 \langle \psi_{l'm}^p | H_0^2 | \psi_{l'm}^{p'} \rangle &= \left\langle \frac{1}{r} \xi^p \begin{pmatrix} \mathcal{U}_{l+1}^m \\ 0 \end{pmatrix} \middle| H_0^2 \middle| \frac{1}{r} \xi^{p'} \begin{pmatrix} \mathcal{U}_{l+1}^{m'} \\ 0 \end{pmatrix} \right\rangle \\
 &= \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty r \xi^p(r) \left\{ c^2 \left(\frac{-\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)\hbar^2}{r^2} \right) + (mc^2)^2 + v^2(r) + 2mc^2 v(r) \right\} \frac{1}{r} \xi^{p'}(r) dr \\
 &= \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty r^{2+p+1} e^{-\lambda r} \left\{ (\hbar c)^2 \left(-\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{r^2} \right) + (mc^2)^2 + v^2(r) + 2mc^2 v(r) \right\} r^{2+p'-1} e^{-\lambda r} dr \\
 &= \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty \left\{ (\hbar c)^2 [l(l+1) - (2+p')(2+p'-1)] r^{-2} + 2\lambda(2+p') r^{-1} - \lambda^2 \right\} + (mc^2)^2 + v^2(r) \\
 &\quad + 2mc^2 v(r) \Big\} r^{2+p+p'} e^{-2\lambda r} dr
 \end{aligned}$$

$$\begin{aligned}
 \langle \omega_{l'm}^p | H_0^2 | \psi_{l'm}^{p'} \rangle &= \left\langle \frac{1}{r} \xi^p \begin{pmatrix} 0 \\ i \mathcal{U}_{l+1}^m \end{pmatrix} \middle| H_0^2 \middle| \frac{1}{r} \xi^{p'} \begin{pmatrix} \mathcal{U}_{l+1}^m \\ 0 \end{pmatrix} \right\rangle \\
 &= 2\hbar c \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty r \xi^p(r) \left(\sqrt{\frac{2}{\partial r}} + \frac{1}{2} \frac{\partial v}{\partial r} + \frac{\kappa+1}{r} v \right) \frac{1}{r} \xi^{p'}(r) dr \\
 &= 2\hbar c \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty r^{2+p+1} e^{-\lambda r} \left(\sqrt{\frac{2}{\partial r}} + \frac{1}{2} \frac{\partial v}{\partial r} + \frac{\kappa+1}{r} v \right) r^{2+p'-1} e^{-\lambda r} dr \\
 &= 2\hbar c \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty \left\{ (2+p'+\kappa) \frac{v}{r} - \lambda v + \frac{1}{2} \frac{\partial v}{\partial r} \right\} r^{2+p+p'} e^{-2\lambda r} dr \\
 &= \langle \psi_{l'm}^{p'} | H_0^2 | \omega_{l'm}^p \rangle
 \end{aligned}$$

$$\begin{aligned}
 \langle \omega_{l'm}^p | H_0^2 | \omega_{l'm}^{p'} \rangle &= \left\langle \frac{1}{r} \xi^p \begin{pmatrix} 0 \\ i \mathcal{U}_{l+1}^m \end{pmatrix} \middle| H_0^2 \middle| \frac{1}{r} \xi^{p'} \begin{pmatrix} 0 \\ i \mathcal{U}_{l+1}^{m'} \end{pmatrix} \right\rangle \\
 &= \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty r \xi^p(r) \left\{ c^2 \left(\frac{-\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{l^2}{r^2} \right) + (mc^2)^2 + v^2(r) - 2mc^2 v(r) \right\} \frac{1}{r} \xi^{p'}(r) dr \\
 &= \delta_{ll'} \delta_{ll'} \delta_{mm'} \int_0^\infty \left\{ (\hbar c)^2 [l(l+1) - (2+p')(2+p'-1)] r^{-2} + 2\lambda(2+p') r^{-1} - \lambda^2 \right\} + (mc^2)^2 + v^2(r) \\
 &\quad - 2mc^2 v(r) \Big\} r^{2+p+p'} e^{-2\lambda r} dr
 \end{aligned}$$

Again for a hydrogenic system $V(r) = -\frac{Z e^2 \lambda C}{r}$

and the matrix elements of the square of the Hamiltonian are thus given by

$$\begin{aligned} \langle \psi_{l'm}^p | H_0^2 | \psi_{l''m'}^{p'} \rangle &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \int_0^\infty (\hbar c)^2 [\ell(\ell+1) - (\gamma + \rho')(\gamma + \rho' - 1) + (Z\lambda)^2] r^{-2} \\ &\quad + 2\hbar c^2 [\lambda \hbar (\gamma + \rho') - Z\lambda m c] r^{-1} + (m c^2)^2 - (\lambda \hbar c)^2 \} r^{2\gamma + \rho + \rho'} e^{-2\lambda r} dr \\ &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ (\hbar c)^2 [\ell(\ell+1) - (\gamma + \rho')(\gamma + \rho' - 1) + (Z\lambda)^2] \frac{\Gamma(2\gamma + \rho + \rho' - 1)}{(2\lambda)^{2\gamma + \rho + \rho' - 1}} \right. \\ &\quad \left. + 2\hbar c^2 [\lambda \hbar (\gamma + \rho') - Z\lambda m c] \frac{\Gamma(2\gamma + \rho + \rho')}{(2\lambda)^{2\gamma + \rho + \rho'}} + [(m c^2)^2 - (\lambda \hbar c)^2] \frac{\Gamma(2\gamma + \rho + \rho' + 1)}{(2\lambda)^{2\gamma + \rho + \rho' + 1}} \right\} \end{aligned}$$

$$\begin{aligned} \langle \psi_{l'm}^p | H_0^2 | \psi_{l''m'}^{p'} \rangle &= 2Z\lambda (\hbar c)^2 \delta_{jj'} \delta_{ll'} \delta_{mm'} \int_0^\infty \left[\ell^2 - (\gamma + \rho' + \kappa) \right] r^{-2} + \lambda r^{-1} \} r^{2\gamma + \rho + \rho'} e^{-2\lambda r} dr \\ &= 2Z\lambda (\hbar c)^2 \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ \left[\frac{\ell^2}{2} - (\gamma + \rho' + \kappa) \right] \frac{\Gamma(2\gamma + \rho + \rho' - 1)}{(2\lambda)^{2\gamma + \rho + \rho' - 1}} + \lambda \frac{\Gamma(2\gamma + \rho + \rho')}{(2\lambda)^{2\gamma + \rho + \rho'}} \right\} \\ &= \langle \psi_{l''m'}^{p'} | H_0^2 | \psi_{l'm}^p \rangle \end{aligned}$$

$$\begin{aligned} \langle \omega_{l'm}^p | H_0^2 | \omega_{l''m'}^{p'} \rangle &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ (\hbar c)^2 [\ell(\ell+1) - (\gamma + \rho')(\gamma + \rho' - 1) + (Z\lambda)^2] \frac{\Gamma(2\gamma + \rho + \rho' - 1)}{(2\lambda)^{2\gamma + \rho + \rho' - 1}} \right. \\ &\quad \left. + 2\hbar c^2 [\lambda \hbar (\gamma + \rho') + Z\lambda m c] \frac{\Gamma(2\gamma + \rho + \rho')}{(2\lambda)^{2\gamma + \rho + \rho'}} + [(m c^2)^2 - (\lambda \hbar c)^2] \frac{\Gamma(2\gamma + \rho + \rho' + 1)}{(2\lambda)^{2\gamma + \rho + \rho' + 1}} \right\} \end{aligned}$$

Hence the matrix elements of H_0^2 in the STO basis are given by

$$\begin{aligned} \langle \hat{\psi}_{l'm}^p | H_0^2 | \hat{\psi}_{l''m'}^{p'} \rangle &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ (\hbar c)^2 [\ell(\ell+1) - (\gamma + \rho')(\gamma + \rho' - 1) + (Z\lambda)^2] \frac{4\lambda^2}{(2\gamma + \rho + \rho')(2\gamma + \rho + \rho' - 1)} \right. \\ &\quad \left. + 4\hbar c^2 \frac{\lambda \hbar (\gamma + \rho') - Z\lambda m c}{2\gamma + \rho + \rho'} + (m c^2)^2 - (\lambda \hbar c)^2 \right\} \omega_{pp'} \\ &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ 4(\lambda \hbar c)^2 \frac{\ell(\ell+1) + (Z\lambda)^2 + (\gamma + \rho')(\gamma + \rho')}{(2\gamma + \rho + \rho')(2\gamma + \rho + \rho' - 1)} - \frac{4\lambda m c^3 Z\lambda \hbar}{2\gamma + \rho + \rho'} + (m c^2)^2 - (\lambda \hbar c)^2 \right\} \omega_{pp'} \end{aligned}$$

$$\begin{aligned} \langle \hat{\omega}_{l'm}^p | H_0^2 | \hat{\omega}_{l''m'}^{p'} \rangle &= 4Z\lambda (\hbar c \lambda)^2 \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ \frac{1 - 2(\gamma + \rho' + \kappa)}{(2\gamma + \rho + \rho')(2\gamma + \rho + \rho' - 1)} + \frac{1}{2\gamma + \rho + \rho'} \right\} \omega_{pp'} \\ &= 4Z\lambda (\lambda \hbar c)^2 \frac{\rho - \rho' - 2\kappa}{(2\gamma + \rho + \rho')(2\gamma + \rho + \rho' - 1)} = \langle \hat{\psi}_{l''m'}^{p'} | H_0^2 | \hat{\psi}_{l'm}^p \rangle \end{aligned}$$

$$\begin{aligned} \langle \hat{\omega}_{l'm}^p | H_0^2 | \hat{\omega}_{l''m'}^{p'} \rangle &= \delta_{jj'} \delta_{ll'} \delta_{mm'} \left\{ 4(\lambda \hbar c)^2 \frac{\ell(\ell+1) + (Z\lambda)^2 + (\gamma + \rho')(\gamma + \rho')}{(2\gamma + \rho + \rho')(2\gamma + \rho + \rho' - 1)} + \frac{4\lambda m c^3 Z\lambda \hbar}{2\gamma + \rho + \rho'} \right. \\ &\quad \left. + (m c^2)^2 - (\lambda \hbar c)^2 \right\} \omega_{pp'} \end{aligned}$$

Orthonormalization.

The STO basis is not orthogonal but rather than orthogonalizing this basis directly, we instead compute the desired matrix elements in the STO Basis and then apply a transformation to the matrices obtained, after the manner of Drake and Goldman, in order to obtain the matrix representation in an orthogonal basis.

Thus suppose U^d is an orthogonal matrix such that

$$\omega_{ki}^d \omega_{kl}^d U_{lj}^d = \Omega_i^d \delta_{ij}$$

i.e. U^d is an orthogonal matrix transforming the overlap matrix to a diagonal matrix, the existence of such a matrix being guaranteed by the symmetry of the overlap matrix, since $\omega^d \in M_{d+1}(\mathbb{R})$ is defined by

$$\omega_{ij}^d = \omega_{ji}^d \quad 0 \leq i, j \leq d$$

If we define \hat{U}^d by

$$\hat{U}_{ij}^d = (\Omega_i^d)^{-\frac{1}{2}} U_{ij}^d$$

(where it is apparent from the above discussion that the Ω_i^d are the eigenvalues of ω^d) then we have that

$$\begin{aligned} \hat{U}_{ki}^d \omega_{kl}^d \hat{U}_{lj}^d &= (\Omega_i^d)^{-\frac{1}{2}} U_{ki}^d \omega_{kl}^d (\Omega_j^d)^{-\frac{1}{2}} U_{lj}^d \\ &= (\Omega_i^d)^{-\frac{1}{2}} (\Omega_j^d)^{-\frac{1}{2}} \Omega_i^d \delta_{ij} \\ &= \delta_{ij} \end{aligned}$$

Thus introducing the functions \hat{x}^p, \hat{y}^p defined by

$$\hat{x}^p = \hat{U}_{q,p}^N \hat{v}^q,$$

$$\hat{y}^p = \hat{U}_{q,p}^M \hat{w}^q$$

we have that

$$\begin{aligned} \langle \hat{x}^p | \hat{x}^{p'} \rangle &= \langle \hat{U}_{q,p}^N \hat{v}^q | \hat{U}_{q',p'}^N \hat{v}^{q'} \rangle \\ &= \hat{U}_{q,p}^N \omega_{q,q'} \hat{U}_{q',p'}^N \\ &= \delta_{pp'} \end{aligned}$$

$$\begin{aligned} \langle \hat{y}^p | \hat{y}^{p'} \rangle &= \langle \hat{U}_{q,p}^M \hat{w}^q | \hat{U}_{q',p'}^M \hat{w}^{q'} \rangle \\ &= \hat{U}_{q,p}^M \omega_{q,q'} \hat{U}_{q',p'}^M \\ &= \delta_{pp'} \end{aligned}$$

and the basis $\beta' \equiv \{ \hat{x}^p, \hat{y}^q / 0 \leq p \leq N, 0 \leq q \leq M \}$ is thus orthonormal.

The matrix elements of an operator A in β' are given in terms of the matrix elements of A in the STO basis by

$$\begin{aligned} \langle \hat{x}^p | A | \hat{x}^{p'} \rangle &= \langle \hat{U}_{q,p}^N \hat{v}^q | A | \hat{U}_{q',p'}^N \hat{v}^{q'} \rangle \\ &= \hat{U}_{q,p}^N \langle \hat{v}^q | A | \hat{v}^{q'} \rangle \hat{U}_{q',p'}^N \quad 0 \leq p, p', q, q' \leq N \end{aligned}$$

$$\begin{aligned} \langle \hat{y}^p | A | \hat{x}^{p'} \rangle &= \langle \hat{U}_{q,p}^M \hat{w}^q | A | \hat{U}_{q',p'}^N \hat{v}^{q'} \rangle \\ &= \hat{U}_{q,p}^M \langle \hat{w}^q | A | \hat{v}^{q'} \rangle \hat{U}_{q',p'}^N \\ &= \langle \hat{x}^{p'} | A | \hat{y}^p \rangle \quad 0 \leq p, q \leq M; 0 \leq p', q' \leq N \end{aligned}$$

$$\begin{aligned} \langle \hat{y}^p | A | \hat{y}^{p'} \rangle &= \langle \hat{U}_{q,p}^M \hat{w}^q | A | \hat{U}_{q',p'}^M \hat{w}^{q'} \rangle \\ &= \hat{U}_{q,p}^M \langle \hat{w}^q | A | \hat{w}^{q'} \rangle \hat{U}_{q',p'}^M \quad 0 \leq p, p', q, q' \leq M \end{aligned}$$

Diagonalization of the matrix representation of H_0^2 in the orthogonal

basis obtained above then yields approximations to the N lowest bound-

state eigenenergies which must be at least as large as those bound-state eigenenergies.

Computation of the Sum Rules

Once the representation of the squared Hamiltonian has been diagonalized the sum rules can be computed. In particular if A is the orthogonal matrix which diagonalizes the representation of H_0^2 in an orthogonal basis then the eigenstates of H_0^2 are given by

$$\begin{aligned} \psi_k &= a_{p_1 k} \hat{x}^{p_1} + a_{p_2 k} \hat{y}^{p_2}, \quad 0 \leq p_1 \leq N, N+1 \leq p_2 \leq N+m+1 \\ &\quad 0 \leq k \leq N+m+1 \\ &= a_{p_1 k} \hat{u}_{q_1 k}^N \hat{v}^{q_1} + a_{p_2 k} \hat{u}_{q_2 k}^M \hat{w}^{q_2} \\ &= b_{q_1 k} \hat{v}^{q_1} + b_{q_2 k} \hat{w}^{q_2} \end{aligned}$$

$$\text{with } b_{qk} \equiv \begin{cases} \hat{u}_{q,p}^N a_{p,k} & 0 \leq q \leq N \\ \hat{u}_{q,p}^M a_{p,k} & N+1 \leq q \leq N+m+1 \end{cases}$$

Thus

$$\begin{aligned} |\langle \psi_k^{i'l'm'} | \hat{r} | \psi_0^{i'l'm} \rangle|^2 &= |\langle b_{q_1 k} \hat{v}_{i'l'm'}^{q_1} + b_{q_2 k} \hat{w}_{i'l'm'}^{q_2} | \hat{r} | b_{q_1 0} \hat{v}_{i'l'm}^{q_1} + b_{q_2 0} \hat{w}_{i'l'm}^{q_2} \rangle|^2 \\ &= |b_{q_1 k} b_{q_1 0} \langle \hat{v}^{q_1} | \hat{r} | \hat{v}^{q_1} \rangle + b_{q_2 k} b_{q_2 0} \langle \hat{w}^{q_2} | \hat{r} | \hat{w}^{q_2} \rangle|^2 \quad (45) \end{aligned}$$

since

$$\begin{aligned} \langle \hat{v}_{i'l'm}^p | x_i | \hat{w}_{i'l'm}^q \rangle &= N_{pp}^{-\frac{1}{2}} N_{qq}^{-\frac{1}{2}} \langle \frac{1}{r} \xi^p \begin{pmatrix} \mathcal{U}_{i'l'}^{m'} \\ 0 \end{pmatrix} | x_i | \frac{1}{r} \xi^q \begin{pmatrix} 0 \\ i \mathcal{U}_{i'l'}^m \end{pmatrix} \rangle \\ &= 0 \\ &= \langle \hat{w}_{i'l'm}^q | x_i | \hat{v}_{i'l'm}^p \rangle \end{aligned}$$

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Multiplying out (45) gives us

$$\begin{aligned}
 |\langle \psi_{\ell}^{j, \ell, m} | \vec{r} | \psi_{\ell'}^{j', \ell', m'} \rangle|^2 &= (b_{\ell, \ell} b_{\ell', 0} \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, \ell}^{j', \ell', m'} \rangle + b_{\ell, 2} b_{\ell', 0} \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, 2}^{j', \ell', m'} \rangle) \\
 &\quad \times (b_{\ell', \ell} b_{\ell, 0} \langle \hat{v}_{\ell', \ell}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', \ell}^{j, \ell, m} \rangle + b_{\ell', 2} b_{\ell, 0} \langle \hat{v}_{\ell', \ell}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', 2}^{j, \ell, m} \rangle) \\
 &= b_{\ell, \ell} b_{\ell', 0} b_{\ell', \ell} b_{\ell, 0} \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, \ell}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', \ell}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', \ell}^{j, \ell, m} \rangle \\
 &\quad + b_{\ell, \ell} b_{\ell', 0} b_{\ell', 2} b_{\ell, 0} \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, 2}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', 2}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', \ell}^{j, \ell, m} \rangle \\
 &\quad + b_{\ell, 2} b_{\ell', 0} b_{\ell', \ell} b_{\ell, 0} \langle \hat{v}_{\ell, 2}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, \ell}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', \ell}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', 2}^{j, \ell, m} \rangle \\
 &\quad + b_{\ell, 2} b_{\ell', 0} b_{\ell', 2} b_{\ell, 0} \langle \hat{v}_{\ell, 2}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, 2}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', 2}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', 2}^{j, \ell, m} \rangle \\
 &= b_{\ell, \ell} b_{\ell', 0} b_{\ell', \ell} b_{\ell, 0} \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, \ell}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', \ell}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', \ell}^{j, \ell, m} \rangle \\
 &\quad + b_{\ell, \ell} b_{\ell', 0} b_{\ell', 2} b_{\ell, 0} \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, 2}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', 2}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', \ell}^{j, \ell, m} \rangle \\
 &\quad + b_{\ell, 2} b_{\ell', 0} b_{\ell', \ell} b_{\ell, 0} \langle \hat{v}_{\ell, 2}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, \ell}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', \ell}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', 2}^{j, \ell, m} \rangle \\
 &\quad + b_{\ell, 2} b_{\ell', 0} b_{\ell', 2} b_{\ell, 0} \langle \hat{v}_{\ell, 2}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell, 2}^{j', \ell', m'} \rangle \cdot \langle \hat{v}_{\ell', 2}^{j', \ell', m'} | \vec{r} | \hat{v}_{\ell', 2}^{j, \ell, m} \rangle
 \end{aligned}$$

since $\langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell', \ell'}^{j', \ell', m'} \rangle = N_{\ell \ell}^{-\frac{1}{2}} N_{\ell' \ell'}^{-\frac{1}{2}} \langle \frac{1}{r} \xi^{\ell} \begin{pmatrix} 0 \\ \ell \end{pmatrix} | \vec{r} | \frac{1}{r} \xi^{\ell'} \begin{pmatrix} 0 \\ \ell' \end{pmatrix} \rangle$

$$\begin{aligned}
 &= N_{\ell \ell}^{-\frac{1}{2}} N_{\ell' \ell'}^{-\frac{1}{2}} \int \frac{\vec{r}}{r^2} \xi^{\ell}(r) \xi^{\ell'}(r) \mathcal{Y}_{\ell \ell}^m \mathcal{Y}_{\ell' \ell'}^{m'} dV \\
 &= N_{\ell \ell}^{-\frac{1}{2}} N_{\ell' \ell'}^{-\frac{1}{2}} \langle \frac{1}{r} \xi^{\ell} \begin{pmatrix} \ell \\ 0 \end{pmatrix} | \vec{r} | \frac{1}{r} \xi^{\ell'} \begin{pmatrix} \ell' \\ 0 \end{pmatrix} \rangle \\
 &= \langle \hat{v}_{\ell, \ell}^{j, \ell, m} | \vec{r} | \hat{v}_{\ell', \ell'}^{j', \ell', m'} \rangle
 \end{aligned}$$

Writing out the scalar products explicitly in terms of the components of r and expressing these components as spherical tensor operators

i.e. $\kappa_i = \sqrt{\frac{4\pi}{3}} r Y_1^i(\hat{r})$

$\Rightarrow \kappa_i^{\dagger} = \sqrt{\frac{4\pi}{3}} r Y_1^{i\dagger}(\hat{r})$

$= (-1)^i \sqrt{\frac{4\pi}{3}} r Y_1^{-i}(\hat{r})$

we obtain

$$\begin{aligned}
 & |\langle \psi_k^{i'l'm'} | \hat{r} | \psi_0^{i'l'm} \rangle|^2 \\
 &= (-1)^i \left\{ b_{q,k} b_{q,0} b_{q,k} b_{q,0} \langle \psi_{i'l'm'}^{q_1} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_1} \rangle \langle \psi_{i'l'm}^{q_1'} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_1} \rangle \right. \\
 &\quad + b_{q,k} b_{q,0} b_{q_2,k} b_{q_2,0} \langle \psi_{i'l'm'}^{q_1} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_1} \rangle \langle \psi_{i'l'm}^{q_2} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_2} \rangle \\
 &\quad + b_{q_2,k} b_{q_2,0} b_{q,k} b_{q,0} \langle \psi_{i'l'm'}^{q_2} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_2} \rangle \langle \psi_{i'l'm}^{q_1} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_1} \rangle \\
 &\quad \left. + b_{q_2,k} b_{q_2,0} b_{q_2,k} b_{q_2,0} \langle \psi_{i'l'm'}^{q_2} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_2} \rangle \langle \psi_{i'l'm}^{q_2} | \frac{4\pi}{3} r Y_i^i(\hat{r}) | \psi_{i'l'm}^{q_2} \rangle \right\} \quad (46)
 \end{aligned}$$

Summing (46) over the final magnetic substates, averaging it over the initial magnetic substates, and exploiting the invariance of (46) under this average due to the spherical symmetry of the system we obtain

$$\begin{aligned}
 \sum_{m'} |\langle \psi_k^{i'l'm'} | \hat{r} | \psi_0^{i'l'm} \rangle|^2 &= \frac{1}{2i+1} \sum_{mm'} |\langle \psi_k^{i'l'm'} | \hat{r} | \psi_0^{i'l'm} \rangle|^2 \\
 &= b_{q,k} b_{q,0} b_{q,k} b_{q,0} R^{q_1' q_1} R^{q_1 q_1} O(i \hat{i} l' l l' l) \\
 &\quad + b_{q,k} b_{q,0} b_{q_2,k} b_{q_2,0} R^{q_1' q_2} R^{q_1 q_2} O(i \hat{i} \hat{l} l' l' l) \\
 &\quad + b_{q_2,k} b_{q_2,0} b_{q,k} b_{q,0} R^{q_2' q_1} R^{q_2 q_1} O(i \hat{i} l' l \hat{l} l) \\
 &\quad + b_{q_2,k} b_{q_2,0} b_{q_2,k} b_{q_2,0} R^{q_2' q_2} R^{q_2 q_2} O(i \hat{i} \hat{l} l' \hat{l} l)
 \end{aligned}$$

where $R^{ij} = N_{ii}^{-\frac{1}{2}} N_{jj}^{-\frac{1}{2}} \int_0^\infty r \xi^i(r) \xi^j(r) dr$

$$= \frac{(2\lambda)^{\gamma+i+\frac{1}{2}} (2\lambda_0)^{\gamma_0+j+\frac{1}{2}}}{(\Gamma(2\gamma+2i+1)\Gamma(2\gamma_0+2j+1))^{\frac{1}{2}}} \int_0^\infty r^{\gamma+\gamma_0+i+j-1} e^{-(\lambda+\lambda_0)r} dr$$

$$= \frac{(2\lambda)^{\gamma+i+\frac{1}{2}} (2\lambda_0)^{\gamma_0+j+\frac{1}{2}}}{(\Gamma(2\gamma+2i+1)\Gamma(2\gamma_0+2j+1))^{\frac{1}{2}}} \frac{\Gamma(\gamma+\gamma_0+i+j+2)}{(\lambda+\lambda_0)^{\gamma+\gamma_0+i+j+2}}$$

$$= \frac{1}{2} (\gamma+\gamma_0+i+j+1) \frac{(2\lambda)^{\gamma+i+\frac{1}{2}} (2\lambda_0)^{\gamma_0+j+\frac{1}{2}}}{(\lambda+\lambda_0)^{\gamma+\gamma_0+i+j+2}} \frac{\Gamma(\gamma+\gamma_0-1)}{(\Gamma(2\gamma-1)\Gamma(2\gamma_0-1))^{\frac{1}{2}}} \frac{\prod_{l=0}^{i+j-(2n+1)} \frac{\gamma+\gamma_0+i+j-l}{(\gamma+n-l_1)(\gamma_0+n-l_2-1)}}{\prod_{l=0}^{2n+1} \frac{\gamma+\gamma_0+2n-l}{(\gamma+n-l_1)(\gamma_0+n-l_2)}}^{\frac{1}{2}}$$

$$n' \equiv \max \{i, j\}$$

$$n \equiv \min \{i, j\}$$

$$\gamma' \equiv \begin{cases} \gamma & i > j \\ \gamma_0 & i < j \end{cases}$$

and $\mathcal{O}(i, j, l_2', l_2, l_1', l_1) = \frac{4\pi}{3} \frac{(-1)^i}{2j+1} \left\langle \begin{pmatrix} \gamma_{l_2'}^m \\ 0 \end{pmatrix} \middle| Y_i^{-i} \begin{pmatrix} \gamma_{l_2}^m \\ 0 \end{pmatrix} \right\rangle \left\langle \begin{pmatrix} \gamma_{l_1'}^m \\ 0 \end{pmatrix} \middle| Y_i^i \begin{pmatrix} \gamma_{l_1}^m \\ 0 \end{pmatrix} \right\rangle$

$$= \frac{4\pi}{3} \frac{(-1)^i}{2j+1} \langle \gamma_{l_2}^m | Y_i^{-i} | \gamma_{l_2'}^m \rangle \langle \gamma_{l_1}^m | Y_i^i | \gamma_{l_1'}^m \rangle$$

$$= \frac{4\pi}{3} \frac{(-1)^i}{2j+1} \langle l_2 m_2 \frac{1}{2} \mu_2 | j m \rangle Y_{l_2}^{m_2} \chi^{\mu_2} | Y_i^{-i} | \langle l_2' m_2' \frac{1}{2} \mu_2' | j' m' \rangle Y_{l_2'}^{m_2'} \chi^{\mu_2'} \rangle$$

$$\times \langle \langle l_1' m_1' \frac{1}{2} \mu_1' | j' m' \rangle Y_{l_1'}^{m_1'} \chi^{\mu_1'} | Y_i^i | \langle l_1 m_1 \frac{1}{2} \mu_1 | j m \rangle Y_{l_1}^{m_1} \chi^{\mu_1} \rangle$$

$$= \frac{4\pi}{3} \frac{(-1)^i}{2j+1} \langle l_2 m_2 \frac{1}{2} \mu_2 | j m \rangle \langle l_2' m_2' \frac{1}{2} \mu_2' | j' m' \rangle \langle l_1' m_1' \frac{1}{2} \mu_1' | j' m' \rangle \langle l_1 m_1 \frac{1}{2} \mu_1 | j m \rangle$$

$$\times \langle l_2 m_2 | Y_i^{-i} | l_2' m_2' \rangle \langle l_1' m_1' | Y_i^i | l_1 m_1 \rangle$$

$$= \frac{4\pi}{3} \frac{(-1)^i}{2j+1} \langle l_2 m_2 \frac{1}{2} \mu_2 | j m \rangle \langle l_2' m_2' \frac{1}{2} \mu_2' | j' m' \rangle \langle l_1' m_1' \frac{1}{2} \mu_1' | j' m' \rangle \langle l_1 m_1 \frac{1}{2} \mu_1 | j m \rangle$$

$$\times \langle l_2 m_2 | l_2' m_2' 1-i \rangle \langle l_2 || Y_i || l_2' \rangle \langle l_1' m_1' | l_1 m_1 1-i \rangle \langle l_1' || Y_i || l_1 \rangle$$

But

$$\begin{aligned}
& (-1)^{i'(\ell_2 m_2 + \frac{1}{2} \mu_2 |j m\rangle \langle \ell_2' m_2' + \frac{1}{2} \mu_2 |j' m'\rangle \langle \ell_2' m_2' + \frac{1}{2} \mu_2 |j' m'\rangle \langle \ell_2' m_2' + \frac{1}{2} \mu_2 |j' m'\rangle \langle \ell_2' m_2' + \frac{1}{2} \mu_2 |j' m'\rangle \langle \ell_2' m_2' + \frac{1}{2} \mu_2 |j' m'\rangle \langle \ell_2' m_2' + \frac{1}{2} \mu_2 |j' m'\rangle} \\
& = (-1)^{i+4(j+j')+2(\ell_2'+\ell_2)} (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \\
& \quad \times \text{Diagram 1} \\
& = (-1)^i (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \\
& \quad \times \text{Diagram 2} \\
& = (-1)^i (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \\
& \quad \times \text{Diagram 3} \\
& = (-1)^i (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \\
& \quad \times \text{Diagram 4} \\
& = (-1)^i (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \\
& \quad \times \text{Diagram 5} \\
& = (-1)^{i+(\ell_2+\ell_2'+1)+(j+\frac{1}{2}+\ell_2'+\frac{1}{2}+j'+\frac{1}{2}+\ell_2'+\frac{1}{2})+1-i} \\
& \quad (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & j' & \ell_2' \\ 1 & \ell_2 & i \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & j' & \ell_2' \\ 1 & \ell_1 & i' \end{Bmatrix} \\
& = (-1)^{\ell_2'+\ell_2} (2j+1)(2j'+1)(2\ell_2'+1)^{\frac{1}{2}} (2\ell_2+1)^{\frac{1}{2}} \begin{Bmatrix} 1 & \ell_2 & \ell_2' \\ \frac{1}{2} & j' & i' \end{Bmatrix} \begin{Bmatrix} 1 & \ell_1 & \ell_1' \\ \frac{1}{2} & j & i \end{Bmatrix}
\end{aligned}$$

while

$$\langle l_1' || Y_1 || l_1 \rangle = (-1)^{l_1 - l_1'} \left(\frac{3}{4\pi} [2l_1 + 1] \right)^{1/2} \begin{pmatrix} 1 & l_1 & l_1' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\langle l_2' || Y_1 || l_2 \rangle = (-1)^{l_2 - l_2'} \left(\frac{3}{4\pi} [2l_2 + 1] \right)^{1/2} \begin{pmatrix} 1 & l_2 & l_2' \\ 0 & 0 & 0 \end{pmatrix}$$

and we therefore have that^{18,19}

$$\begin{aligned} \delta_{l_1' l_2' l_2 l_1} &= (2j' + 1) [2l_1 + 1] [2l_1' + 1] [2l_2 + 1] [2l_2' + 1]^{1/2} \begin{pmatrix} 1 & l_1 & l_1' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & l_2 & l_2' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1' \\ l_2 & l_2' \end{pmatrix} \\ &= (2j' + 1) \begin{pmatrix} j' & j & 1 \\ j_2 & -j_2 & 0 \end{pmatrix}^2 \end{aligned}$$

Thus (47) becomes

$$\begin{aligned} \sum_m |\langle \psi_{j' l_1' m'} | \vec{r} | \psi_{j l_2 m} \rangle|^2 &= \delta(j' j) \left\{ b_{j_1 k} b_{j_1' 0} b_{j_2 k} b_{j_2' 0} R^{j_1' j_1''} R^{j_2 j_2''} \right. \\ &\quad + b_{j_1 k} b_{j_1' 0} b_{j_2 k} b_{j_2' 0} R^{j_1' j_2''} R^{j_2 j_1''} \\ &\quad + b_{j_1 k} b_{j_2' 0} b_{j_2 k} b_{j_1' 0} R^{j_1' j_1''} R^{j_2 j_2''} \\ &\quad \left. + b_{j_1 k} b_{j_2' 0} b_{j_2 k} b_{j_1' 0} R^{j_1' j_2''} R^{j_2 j_1''} \right\} \\ &= \delta(j' j) \left\{ C_{k0} b_{j_1 k} R^{j_1' j_1''} b_{j_1' 0} + C_{k0} b_{j_2 k} R^{j_2' j_2''} b_{j_2' 0} \right\} \\ &= \delta(j' j) C_{k0}^2, \quad C \equiv b^{\dagger} R b \end{aligned}$$

and the sums in (12) can be computed directly from

$$\begin{aligned} S_k &\equiv \frac{2}{3} \sum_j (E_j - E_0)^k |\langle \psi_0 | \vec{r} | \psi_j \rangle|^2 \\ &= \frac{2}{3} \sum_j \sum_{j' l_1' m'} (E_{j'} - E_0)^k |\langle \psi_0^{j l_2 m} | \vec{r} | \psi_{j' l_1' m'} \rangle|^2 \\ &= \frac{2}{3} \sum_j \sum_{j' l_1'} (E_{j'} - E_0)^k \delta(j' j) C_{k0}^2 \end{aligned}$$

where the range of the final angular momentum quantum numbers is determined by the selection rules for the matrix element

$\langle \psi_{j' l' m'} | \vec{r} | \psi_{j l m} \rangle$ or equivalently for the $3-j$ symbol in $\delta(j', j)$ taking into consideration explicitly the fact that the initial and final states must have opposite parity.

Thus we have that $|j - j'| \leq 1 \Rightarrow j' = j, j \pm 1$

Hence if $(j, l) = (\frac{1}{2}, 0)$

then $j' = \begin{cases} \frac{1}{2} \Rightarrow l' = 1 \Rightarrow \kappa = 1 \\ \frac{3}{2} \Rightarrow l' = 1 \Rightarrow \kappa = -2 \end{cases}$

$$\delta(\frac{1}{2}, \frac{1}{2}) = 2 \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix}^2 = 2 \frac{\frac{1}{4}}{(\frac{1}{2})(\frac{3}{2})(2)} = \frac{1}{3}$$

$$\delta(\frac{3}{2}, \frac{1}{2}) = 4 \begin{pmatrix} \frac{3}{2} & \frac{1}{2} & 1 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix}^2 = 4 \frac{2(1)}{(\frac{3}{2})(2)(4)} = \frac{2}{3}$$

Results and Discussion

In the calculations above employing a two-dimensional variational subspace, we see that optimization of $\langle H_0^2 \rangle$ avoids the indeterminacy in the variational eigenfunction symptomatic of Drake and Goldman's method, essentially through the inclusion of a term involving $\langle \frac{1}{r} \rangle$ in the variational functional \tilde{E} . In addition the eigenvalues obtained for $\kappa < 0$ were exact while those for $\kappa > 0$ exceeded the actual values, and by less than one part in 10^5 , as evidenced in Table 1.

In numerical calculations using the same bases as Drake and Goldman (but relaxing the constraint that the number of positive energy states equal the number of negative energy states in the basis) the analytic eigenenergies were observed to be lower bounds to the variational energies obtained, and these variational solutions were in slightly better agreement with the analytic values than were those of Drake and Goldman. The sum rules computed from the variational solutions of Drake and Goldman, on the other hand, were considerably more accurate than were those obtained in our computations, particularly for those sum rules involving positive powers of the energy differences. This is a consequence of the discrepancy between the eigenfunctions of the representations of H_0 and H_0^2 in a finite-dimensional variational subspace. The higher variational states obtained are less accurate, and as the corresponding energy differences are also greater the sum rules with positive powers of those energy differences will be most affected.

Since the variational solutions obtained in our computations are eigenfunctions of $\rho H_0^2 \rho$ we would expect that direct computations of the modified sum rules

$$\tilde{S}_2 \equiv \sum_j (E_j^2 - E_0^2) |\langle \psi_j | \vec{r} | \psi_0 \rangle|^2 = S_2 + 2E_0 S_1$$

$$\tilde{S}_4 \equiv \sum_j (E_j^4 - E_0^4) |\langle \psi_j | \vec{r} | \psi_0 \rangle|^2 = S_4 + 4E_0 S_3 + 6E_0^2 S_2 + 4E_0^3 S_1$$

from our variational solutions should give good agreement with the analytic values, and this is indeed the case. The values computed for the dipole polarizability, which is given by a sum over inverse powers of the energy differences, agrees with those obtained by Drake and Goldman to as many as five figures. These values are subject to rather severe fluctuations with changing basis size, however, these fluctuations sparing only the first two figures in the values quoted. This would indicate that our lower-lying variational eigenstates are reasonably accurate approximations to the analytic eigenstates. Clearly a more direct and reliable measure of the quality of the variational approximations to the bound-state eigenfunctions would be to compute the overlap of the variational solutions with the analytic bound-state eigenfunctions which they are presumed to approximate.

It would appear from the discussion above that the application of the Ritz variational method to the squared Dirac Hamiltonian affords a means of obtaining stable variational solutions to the Dirac equation, and in particular to systems described by non-spherical potentials. Thus one-electron orbitals with positive-energy states can be obtained in the independent-particle model, from which can be constructed a

basis of many-electron states in the form of Slater determinants of the one-electron orbitals. The Dirac Hamiltonian can thus be diagonalized in this many-electron basis, to give the energies and wave functions of the entire system. The construction of the many-electron states from positive-energy orbitals obviates the introduction of the projection operators prevalent in many of the approaches to this problem currently being pursued.

Table 1

Variational Eigenvalues Obtained for $K=0$ in Two-Dimensional
Variational Subspace Through the Optimization of $\langle H_0 \rangle$

K	A	$E_{\text{mc}}^2 - 1 \quad (10^{-6} \text{ au})$	
		Numerical	Analytic
1	2.509020236	-13.312698	-13.313017
2	3.499999213	-5.916801	-5.916850
3	4.166663812	-3.328206	-3.328214
4	5.124996749	-2.130053	-2.130055
5	6.099996856	-1.479204	-1.479205
6	7.083330409	-1.086762	-1.086763

a) Obtained numerically as a root of (40).

Table 2

Variational Eigenvalues for lowest three $S_{1/2}$ states.

Basis Size		$E - mc^2$ (10^2 au)		
# of positive energy states	# of negative energy states	$1S_{1/2}$	$2S_{1/2}$	$3S_{1/2}$
3	0	-19.2752959645068	-4.82774935411317	8.64646667659135
	1	-20.0133011195827	-4.94988639594885	7.73223797220143
	2	-20.0783589541027	-4.96138919282912	7.01734566188407
	3	-20.0818684689920	-4.95690766258935	7.01490241713655
5	0	-19.2787069103124	-4.90246398654563	-1.63505527548723
	1	-20.0302135540920	-5.01748209514035	-1.72034818523825
	2	-20.1021656012756	-5.03004885326318	-1.73592820476479
	3	-20.1072375352640	-5.03318309512979	-1.73839364785226
	5	-20.1075489609548	-5.03343502812641	-1.74095648162329
14	0	-19.2862135138266	-4.90323165571081	-2.19277958689427
	1	-20.0308128539409	-5.01768102510532	-2.22633212210585
	2	-20.1022296407535	-5.03033275017851	-2.23159557103163
	3	-20.1073210983052	-5.03339755286779	-2.23359322771403
	14	-20.1076523196246	-5.03365942127730	-2.23417619822340
18	0	-19.2870993745068	-4.90333803280319	-2.19280741333887
	1	-20.0309068265646	-5.01758440501219	-2.22633341597848
	2	-20.1022365673096	-5.03033410916978	-2.23159836557661
	3	-20.1073215267084	-5.03339767598027	-2.23359416313733
	18	-20.1076523196246	-5.03365942127730	-2.23417722767072
Analytic Values:		-20.1076523196249	-5.03365942127730	-2.23417722844079

Table 3

Variational Eigenvalues for Lowest Three $P_{1/2}$ States,

Basis Size		$E - mc^2$ (10 au)		
# of positive energy states	# of negative energy states	$2P_{1/2}$	$3P_{1/2}$	$4P_{1/2}$
3	0	-4.93433080545783	2.85813435374248	164.568281841523
	1	-4.99819424719317	2.67886398052197	35.9767344961798
	2	-4.99925729502793	2.59429286883487	15.2472915671185
	3	-5.00021736783601	2.59205885100819	9.37021689141084
5	0	-4.97124505121201	-1.85053019127545	3.31136921545531
	1	-5.03186626892239	-1.88017268590838	3.22654194775596
	2	-5.03292650843223	-1.88699302382120	3.19112559724290
	3	-5.03350318730900	-1.89025569587693	3.18612591693973
	5	-5.03356191728926	-1.89091429027585	3.16902680295898
14	0	-4.97135023600649	-2.21306863135096	-1.24080904467282
	1	-5.03196445159019	-2.22872174301338	-1.24750639809745
	2	-5.03302781414704	-2.23187659248142	-1.24925390015433
	3	-5.03360005411081	-2.23391917079034	-1.25002031357099
	14	-5.03365942127730	-2.23417662949878	-1.25068589758666
18	0	-4.97135029808815	-2.21306928630220	-1.24589098152692
	1	-5.03196445182202	-2.22872236106723	-1.25231485312870
	2	-5.03302781553739	-2.23187725142770	-1.25398981699773
	3	-5.03360005937766	-2.23391975362119	-1.25472931893146
	18	-5.03365942127730	-2.23417722799295	-1.25536485358489
Analytic Values:		-5.03365942127730	-2.23417722844079	-1.25545908910044

Table 4

Variational Eigenvalues for Lowest Three $P_{3/2}$ States,

Basis Size		E-mc ² (10 au)		
# of positive energy states	# of negative energy states	$1P_{3/2}$	$2P_{3/2}$	$3P_{3/2}$
3	0	-4.96873851766168	-.974456133709555	14.2209077686269
	1	-5.00133652868544	-1.01177955338417	13.7814132810718
	2	-5.00424929180163	-1.01357886536225	13.7156160562157
	3	-5.00447577441428	-1.02202840340296	9.14887305723160
5	0	-4.97133925709259	-2.10084370780050	7.47077990142589
	1	-5.00347344800166	-2.11554263731814	7.09265165505258
	2	-5.00648621529517	-2.11618590615826	7.09180089506481
	3	-5.00666179212221	-2.11692148300645	7.05055952362272
	5	-5.00666993225223	-2.11830283604777	6.99549352883878
14	0	-4.97135018308609	-2.21306908533315	-1.24400204402446
	1	-5.00347661116630	-2.22436018096369	-1.24895307778110
	2	-5.00649138286835	-2.22477610143678	-1.24903522110189
	3	-5.00666588241320	-2.22512068474462	-1.24945722830971
	14	-5.00667420160016	-2.22617798577603	-1.25020531506252
18	0	-4.97135027040176	-2.21306927512578	-1.24597205049467
	1	-5.00347664585097	-2.22436026955083	-1.25084238519185
	2	-5.00649138726676	-2.22477619890415	-1.25091621215106
	3	-5.00666588276290	-2.22512081978875	-1.25132729682246
	18	-5.00667420160016	-2.22617908642463	-1.25206190826157
Analytic Values:		-5.00667420160016	-2.22617808646701	-1.25208596626690

Table 5Sum Rules: Relative Error in Computed Values

	Z = 1	Z = 50
$\tilde{Z}^* S_{-1}$	2.021×10^{-5}	-5.606×10^{-4}
S_0	1.914×10^{-7}	1.558×10^{-7}
S_1	-4.877×10^{-1}	-3.382×10^{-1}
S_2	4.877×10^{-1}	3.346×10^{-1}
S_3	-4.877×10^{-1}	-3.380×10^{-1}
S_4	4.877×10^{-1}	3.386×10^{-1}
\tilde{S}_2	4.793×10^{-7}	-3.067×10^{-5}
\tilde{S}_4	3.775×10^{-8}	-4.056×10^{-4}

- a) As computed in a 16-dimensional variational subspace of the type employed by Drake and Goldman. (As was already mentioned, fluctuations in the values obtained for S_{-1} , spared only the first two figures.)
- b) For S_1 (whose analytic value is zero) we computed the absolute error.
- c) For \tilde{S}_{-1} we report the relative discrepancy between our values and those obtained by Drake and Goldman.

Appendix: The Mark-Schwarz Method⁶

Mark and Schwarz address the variational instability due to the inadequate representation of the kinetic energy operator through the introduction of a variational basis $\beta \equiv \{\psi_i(\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}), \dots, \psi_N(\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}), \psi_i(\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}), \dots, \psi_N(\begin{smallmatrix} 0 \\ 1 \end{smallmatrix})\}$ where the ψ_i are two-component spinors and the $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ indicate positive and negative energy states, respectively. Now, since

$$H_D \begin{pmatrix} \psi_i \\ 0 \end{pmatrix} = (mc^2 + v) \begin{pmatrix} \psi_i \\ 0 \end{pmatrix} + c \vec{\sigma} \cdot \vec{p} \begin{pmatrix} 0 \\ \psi_i \end{pmatrix}$$

$$H_D \begin{pmatrix} 0 \\ \psi_i \end{pmatrix} = c \vec{\sigma} \cdot \vec{p} \begin{pmatrix} \psi_i \\ 0 \end{pmatrix} + (-mc^2 + v) \begin{pmatrix} 0 \\ \psi_i \end{pmatrix}$$

we have that

$$\langle \begin{pmatrix} \psi_i \\ 0 \end{pmatrix} | H_D | \begin{pmatrix} \psi_j \\ 0 \end{pmatrix} \rangle = \langle \psi_i | mc^2 + v | \psi_j \rangle$$

$$\langle \begin{pmatrix} 0 \\ \psi_i \end{pmatrix} | H_D | \begin{pmatrix} \psi_j \\ 0 \end{pmatrix} \rangle = c \langle \psi_i | \vec{\sigma} \cdot \vec{p} | \psi_j \rangle$$

$$\langle \begin{pmatrix} \psi_i \\ 0 \end{pmatrix} | H_D | \begin{pmatrix} 0 \\ \psi_j \end{pmatrix} \rangle = c \langle \psi_i | \vec{\sigma} \cdot \vec{p} | \psi_j \rangle$$

$$\langle \begin{pmatrix} 0 \\ \psi_i \end{pmatrix} | H_D | \begin{pmatrix} 0 \\ \psi_j \end{pmatrix} \rangle = \langle \psi_i | -mc^2 + v | \psi_j \rangle$$

and the representation of the Dirac Hamiltonian in this basis thus has the decomposition

$$[H]_{\beta} = \begin{pmatrix} [v + mc^2]_{\chi} & c [\vec{\sigma} \cdot \vec{p}]_{\chi} \\ c [\vec{\sigma} \cdot \vec{p}]_{\chi} & [v - mc^2]_{\chi} \end{pmatrix} \quad (A1)$$

where

$$\chi \equiv \{\psi_1, \dots, \psi_N\}$$

Mark and Schwarz further propose to replace the representation of $\vec{\sigma} \cdot \vec{p}$ in α with a matrix $[\vec{\sigma} \cdot \vec{p}]_{ms}$ satisfying

$$[\vec{\sigma} \cdot \vec{p}]_{ms}^2 = [p^2]_s$$

corresponding to the operator identity

$$(\vec{\sigma} \cdot \vec{p})^2 = p^2$$

In particular Mark and Schwarz replace $[\vec{\sigma} \cdot \vec{p}]_s$ with the matrix

$$[\vec{\sigma} \cdot \vec{p}]_{ms} = [\vec{\sigma} \cdot \vec{p}]_s ([\vec{\sigma} \cdot \vec{p}]_s^{-1} [p^2]_s [\vec{\sigma} \cdot \vec{p}]_s^{-1})^{1/2}$$

Now, taking $\psi_1 = \frac{1}{2} q(r) u_{1\frac{1}{2}}^m$, $\psi_2 = \frac{1}{2} q(r) u_{1\frac{1}{2}}^m$ and

recalling that

$$\vec{\sigma} \cdot \vec{p} u_{1\frac{1}{2}}^m = i\hbar u_{1\frac{1}{2}}^m \left(\frac{1}{r} \frac{\partial}{\partial r} r + \frac{\kappa}{r} \right)$$

$$\vec{\sigma} \cdot \vec{p} u_{1\frac{1}{2}}^m = i\hbar u_{1\frac{1}{2}}^m \left(\frac{1}{r} \frac{\partial}{\partial r} r - \frac{\kappa}{r} \right)$$

we have

$$\langle \psi_1 | \sqrt{\pm mc^2} | \psi_1 \rangle = \langle \psi_1 | \sqrt{\pm mc^2} | \psi_1 \rangle = \langle \psi_2 | \sqrt{\pm mc^2} | \psi_2 \rangle$$

$$\langle \psi_1 | \sqrt{\pm mc^2} | \psi_2 \rangle = 0 = \langle \psi_2 | \sqrt{\pm mc^2} | \psi_1 \rangle$$

and

$$\langle \psi_1 | \vec{\sigma} \cdot \vec{p} | \psi_1 \rangle = 0 = \langle \psi_2 | \vec{\sigma} \cdot \vec{p} | \psi_2 \rangle$$

$$\langle \psi_1 | \vec{\sigma} \cdot \vec{p} | \psi_2 \rangle = i\hbar \left\langle \frac{\partial}{\partial r} - \frac{\kappa}{r} \right\rangle = -i\hbar \kappa \left\langle \frac{1}{r} \right\rangle$$

$$\langle \psi_2 | \vec{\sigma} \cdot \vec{p} | \psi_1 \rangle = i\hbar \left\langle \frac{\partial}{\partial r} + \frac{\kappa}{r} \right\rangle = i\hbar \kappa \left\langle \frac{1}{r} \right\rangle$$

where

$$\langle f(r) \rangle \equiv \int_0^\infty q(r) f(r) q(r) dr$$

Thus

$$[v \pm mc^2]_r = \begin{pmatrix} \langle v \rangle \pm mc^2 & 0 \\ 0 & \langle v \rangle \pm mc^2 \end{pmatrix}$$

$$[\vec{\sigma} \cdot \vec{p}]_r = \begin{pmatrix} 0 & -i\hbar \kappa \langle \frac{1}{r} \rangle \\ i\hbar \kappa \langle \frac{1}{r} \rangle & 0 \end{pmatrix}$$

and

$$[H]_\beta = \begin{pmatrix} \langle v \rangle + mc^2 & 0 & 0 & -i\hbar \kappa \langle \frac{1}{r} \rangle \\ 0 & \langle v \rangle + mc^2 & i\hbar \kappa \langle \frac{1}{r} \rangle & 0 \\ 0 & -i\hbar \kappa \langle \frac{1}{r} \rangle & \langle v \rangle - mc^2 & 0 \\ i\hbar \kappa \langle \frac{1}{r} \rangle & 0 & 0 & \langle v \rangle - mc^2 \end{pmatrix}$$

$$\therefore |[H]_\beta - \epsilon I| = \begin{vmatrix} \langle v \rangle + mc^2 - \epsilon & 0 & 0 & -i\hbar \kappa \langle \frac{1}{r} \rangle \\ 0 & \langle v \rangle + mc^2 - \epsilon & i\hbar \kappa \langle \frac{1}{r} \rangle & 0 \\ 0 & -i\hbar \kappa \langle \frac{1}{r} \rangle & \langle v \rangle - mc^2 - \epsilon & 0 \\ i\hbar \kappa \langle \frac{1}{r} \rangle & 0 & 0 & \langle v \rangle - mc^2 - \epsilon \end{vmatrix}$$

$$= (\langle v \rangle + mc^2 - \epsilon) [(\langle v \rangle + mc^2 - \epsilon)(\langle v \rangle - mc^2 - \epsilon) - [\hbar \kappa \langle \frac{1}{r} \rangle]^2] (\langle v \rangle - mc^2 - \epsilon) \\ - [\hbar \kappa \langle \frac{1}{r} \rangle]^2 [(\langle v \rangle + mc^2 - \epsilon)(\langle v \rangle - mc^2 - \epsilon) - [\hbar \kappa \langle \frac{1}{r} \rangle]^2]$$

$$= ([\langle v \rangle + mc^2 - \epsilon][\langle v \rangle - mc^2 - \epsilon] - [\hbar \kappa \langle \frac{1}{r} \rangle]^2) ([\langle v \rangle + mc^2 - \epsilon][\langle v \rangle - mc^2 - \epsilon] - [\hbar \kappa \langle \frac{1}{r} \rangle]^2)$$

$$= ([\langle v \rangle - \epsilon]^2 - (mc^2)^2 - [\hbar \kappa \langle \frac{1}{r} \rangle]^2) ([\langle v \rangle - \epsilon]^2 - (mc^2)^2 - [\hbar \kappa \langle \frac{1}{r} \rangle]^2)$$

$$= ([\langle v \rangle - \epsilon]^2 - (mc^2)^2 - [\hbar \kappa \langle \frac{1}{r} \rangle]^2)^2 = 0$$

$$\Rightarrow [\langle v \rangle - \epsilon]^2 - (mc^2)^2 - [\hbar \kappa \langle \frac{1}{r} \rangle]^2 = 0$$

$$\langle v \rangle - \epsilon = \pm ((mc^2)^2 + [\hbar \kappa \langle \frac{1}{r} \rangle]^2)^{\frac{1}{2}}$$

Thus the eigenenergies obtained from the diagonalization of the representation of the Dirac Hamiltonian in the basis β are given by

$$E_{\beta} = \langle v \rangle \pm (mc^2 + (\hbar c \kappa \langle \frac{1}{r} \rangle)^2)^{1/2}$$

Observe that in the non-relativistic limit

$$E_{\beta} \rightarrow \langle v \rangle \pm mc^2 (1 + \frac{1}{2} \kappa^2 \left(\frac{\hbar}{mc} \right)^2 \langle r^{-1} \rangle^2)$$

Now,

$$[\vec{\sigma} \cdot \vec{p}]_{\chi}^{-1} = (i \hbar c \kappa \langle \frac{1}{r} \rangle)^{-1} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}^{-1} = i (\hbar c \kappa \langle \frac{1}{r} \rangle)^{-1} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

$$\text{and } \langle \psi_1 | p^2 | \psi_1 \rangle = \langle \psi_1 | -\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2}{r^2} | \psi_1 \rangle = \hbar^2 \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \rangle$$

$$\langle \psi_1 | p^2 | \psi_2 \rangle = 0 = \langle \psi_2 | p^2 | \psi_1 \rangle$$

$$\langle \psi_2 | p^2 | \psi_2 \rangle = \langle \psi_2 | -\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2}{r^2} | \psi_2 \rangle = \hbar^2 \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \rangle$$

$$\Rightarrow [p^2]_{\chi} = \hbar^2 \begin{pmatrix} \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \rangle & 0 \\ 0 & \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \rangle \end{pmatrix}$$

Carrying out the prescription of Mark and Schwarz we now replace

$[\vec{\sigma} \cdot \vec{p}]_{\alpha}$ with the matrix

$$[\vec{\sigma} \cdot \vec{p}]_{m_s} = [\vec{\sigma} \cdot \vec{p}]_{\chi} ([\vec{\sigma} \cdot \vec{p}]_{\chi}^{-1} [p^2]_{\chi} [\vec{\sigma} \cdot \vec{p}]_{\chi}^{-1})^{1/2}$$

$$= \hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \rangle & 0 \\ 0 & \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \rangle \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}^{1/2}$$

$$= \hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \rangle^{1/2} & 0 \\ 0 & \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \rangle^{1/2} \end{pmatrix}$$

$$= \hbar \begin{pmatrix} 0 & -i \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \rangle^{1/2} \\ i \langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \rangle^{1/2} & 0 \end{pmatrix}$$

in (A1) to obtain the modified representation

$$[H_D]_{MS} = \begin{pmatrix} [V + mc^2]_c & c[\vec{\sigma} \cdot \vec{p}]_{MS} \\ c[\vec{\sigma} \cdot \vec{p}]_{MS} & [V - mc^2]_c \end{pmatrix}$$

$$= \begin{pmatrix} \langle V \rangle + mc^2 & 0 & 0 & -i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle^{\frac{1}{2}} \\ 0 & \langle V \rangle + mc^2 & i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle^{\frac{1}{2}} & 0 \\ 0 & -i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle^{\frac{1}{2}} & \langle V \rangle - mc^2 & 0 \\ i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle^{\frac{1}{2}} & 0 & 0 & \langle V \rangle - mc^2 \end{pmatrix}$$

for the Dirac Hamiltonian.

$$\therefore | [H_D]_{MS} - \epsilon |$$

$$= \begin{pmatrix} \langle V \rangle + mc^2 - \epsilon & 0 & 0 & -i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle^{\frac{1}{2}} \\ 0 & \langle V \rangle + mc^2 - \epsilon & i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle^{\frac{1}{2}} & 0 \\ 0 & -i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle^{\frac{1}{2}} & \langle V \rangle - mc^2 - \epsilon & 0 \\ i\hbar c \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle^{\frac{1}{2}} & 0 & 0 & \langle V \rangle - mc^2 - \epsilon \end{pmatrix}$$

$$= [(\langle V \rangle - \epsilon)^2 - (mc^2)^2] \left[(\langle V \rangle - \epsilon)^2 - (mc^2)^2 - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle \right] \\ - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle [(\langle V \rangle - \epsilon)^2 - (mc^2)^2 - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle]$$

$$= [(\langle V \rangle - \epsilon)^2 - (mc^2)^2 - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle] [(\langle V \rangle - \epsilon)^2 - (mc^2)^2 - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle]$$

$$= 0$$

$$\Rightarrow (\langle V \rangle - \epsilon)^2 - (mc^2)^2 - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle = 0 \quad \text{or} \quad (\langle V \rangle - \epsilon)^2 - (mc^2)^2 - (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle = 0$$

$$\langle V \rangle - \epsilon = \pm \left((mc^2)^2 + (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa-1)}{r^2} \right\rangle \right)^{\frac{1}{2}} \quad \langle V \rangle - \epsilon = \pm \left((mc^2)^2 + (\hbar c)^2 \left\langle \frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa+1)}{r^2} \right\rangle \right)^{\frac{1}{2}}$$

Thus the eigenenergies obtained from the Mark-Schwarz method are given by

$$E_{mS} = \langle v \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \left\langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa \pm 1)}{r^2} \right\rangle \right)^{\frac{1}{2}}$$

In the non-relativistic limit

$$E_{mS} \rightarrow \langle v \rangle \pm mc^2 \left(1 + \frac{1}{2} \left(\frac{\hbar}{mc} \right)^2 \left\langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa \pm 1)}{r^2} \right\rangle \right) = \begin{cases} mc^2 + \frac{1}{2} \left(\frac{\hbar}{mc} \right)^2 \left\langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa \pm 1)}{r^2} \right\rangle + \langle v \rangle \\ -mc^2 - \frac{1}{2} \left(\frac{\hbar}{mc} \right)^2 \left\langle -\frac{\partial^2}{\partial r^2} + \frac{\kappa(\kappa \pm 1)}{r^2} \right\rangle + \langle v \rangle \end{cases}$$

Prescribing the radial dependence of the basis functions by

$$\psi(r) = N r^{\alpha_1} e^{-\alpha_2 r} \quad \text{we have for a hydrogenic system}$$

$$V(r) = -\frac{Z e^2 \hbar c}{r}$$

$$\Rightarrow \langle v \rangle = -Z e^2 \hbar c \langle r^{-1} \rangle = -Z e^2 \hbar c \rho \langle r^{-2} \rangle, \quad \rho \equiv \frac{\langle r^{-1} \rangle}{\langle r^{-2} \rangle}$$

$$\text{and } \langle r^{-1} \rangle = N^2 \int_0^\infty r^{2\alpha_1 - 1} e^{-2\alpha_2 r} dr = N^2 \frac{\Gamma(2\alpha_1)}{(2\alpha_2)^{2\alpha_1}}$$

$$\langle r^{-2} \rangle = N^2 \int_0^\infty r^{2\alpha_1 - 2} e^{-2\alpha_2 r} dr = N^2 \frac{\Gamma(2\alpha_1 - 1)}{(2\alpha_2)^{2\alpha_1 - 1}}$$

$$\text{Thus } \rho \equiv \frac{\langle r^{-1} \rangle}{\langle r^{-2} \rangle}$$

$$= \frac{2\alpha_1 - 1}{2\alpha_2}$$

$$\left\langle \frac{\partial^2}{\partial r^2} \right\rangle = N^2 \int_0^\infty r^{\alpha_1} e^{-\alpha_2 r} \frac{\partial^2}{\partial r^2} r^{\alpha_1} e^{-\alpha_2 r} dr$$

$$= N^2 \int_0^\infty \left\{ \alpha_1(\alpha_1 - 1) r^{2\alpha_1 - 2} - 2\alpha_1 \alpha_2 r^{2\alpha_1 - 1} + \alpha_2^2 r^{2\alpha_1} \right\} e^{-2\alpha_2 r} dr$$

$$= \alpha_1(\alpha_1 - 1) \langle r^{-2} \rangle - 2\alpha_1 \alpha_2 \langle r^{-1} \rangle + \alpha_2^2 N^2 \frac{\Gamma(2\alpha_1 + 1)}{(2\alpha_2)^{2\alpha_1 + 1}}$$

$$= \langle r^{-2} \rangle \left\{ \alpha_1(\alpha_1 - 1) - 2\alpha_1 \alpha_2 \frac{2\alpha_1 - 1}{2\alpha_2} + \alpha_2^2 \frac{2\alpha_1(2\alpha_1 - 1)}{(2\alpha_2)^2} \right\}$$

$$= -\frac{1}{2} \alpha_1 \langle r^{-2} \rangle$$

Imposing the normalization

$$\langle 1 \rangle = 1$$

gives us

$$N^2 \int_0^\infty r^{2\alpha_1} e^{-2\alpha_2 r} dr = N^2 \frac{\Gamma(2\alpha_1+1)}{(2\alpha_2)^{2\alpha_1+1}} = 1 \Rightarrow N^2 = \frac{(2\alpha_2)^{2\alpha_1+1}}{\Gamma(2\alpha_1+1)}$$

$$\text{Thus } \langle r^{-2} \rangle \rho^2 = \frac{(2\alpha_2)^{2\alpha_1+1}}{\Gamma(2\alpha_1+1)} \frac{\Gamma(2\alpha_1-1)}{(2\alpha_2)^{2\alpha_1-1}} \frac{2\alpha_1-1}{2\alpha_2} = \frac{(2\alpha_1-1)^2}{2\alpha_1(2\alpha_1-1)} = \frac{2\alpha_1-1}{2\alpha_1}$$

$$\Rightarrow 2\alpha_1 \langle r^{-2} \rangle \rho^2 = 2\alpha_1 - 1$$

$$\alpha_1 = \frac{1}{2} \frac{1}{1 - \rho^2 \langle r^{-2} \rangle}$$

$$\Rightarrow \left\langle \frac{\partial^2}{\partial r^2} \right\rangle = -\frac{1}{2} \frac{\langle r^{-2} \rangle}{1 - \rho^2 \langle r^{-2} \rangle}$$

and finally we arrive at

$$\begin{aligned} E_{ns} &= -Z\alpha\hbar c \rho \langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \left\{ \frac{1}{2} \frac{\langle r^{-2} \rangle}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \langle r^{-2} \rangle \right\} \right)^{1/2} \\ &= -Z\alpha\hbar c \rho \langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle \left\{ \frac{1}{2} \frac{1}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right\} \right)^{1/2} \end{aligned}$$

$$\text{Since } \rho = \frac{2\alpha_1-1}{2\alpha_2}$$

$$\langle r^{-2} \rangle = \frac{(2\alpha_2)^{2\alpha_1+1}}{\Gamma(2\alpha_1+1)} \frac{\Gamma(2\alpha_1-1)}{(2\alpha_2)^{2\alpha_1-1}} = \frac{2\alpha_2^2}{\alpha_1(2\alpha_1-1)}$$

we have that

$$\frac{\partial(\rho, \langle r^{-2} \rangle)}{\partial(\alpha_1, \alpha_2)} = \begin{vmatrix} \frac{1}{2\alpha_2} & -\frac{2\alpha_1-1}{2\alpha_2^2} \\ -2\left(\frac{\alpha_2}{\alpha_1}\right)^2 \frac{4\alpha_1-1}{(2\alpha_1-1)^2} & \frac{4\alpha_2}{\alpha_1(2\alpha_1-1)} \end{vmatrix}$$

$$= \frac{4}{\alpha_1(2\alpha_1-1)} - \frac{4\alpha_1-1}{\alpha_1^2(2\alpha_1-1)}$$

$$= \frac{1}{\alpha_1^2(2\alpha_1-1)} \neq 0 \quad (\forall \alpha_1 \in \mathbb{R} - \{\frac{1}{2}\})$$

and we can therefore treat $\rho, \langle r^{-2} \rangle$ as the independent variables and optimize E_{ms} with respect to them, giving us the equations

$$\frac{\partial E_{ms}}{\partial \langle r^{-2} \rangle} = -2\kappa \hbar c \rho \pm \frac{1}{2} m c^2 \left(1 + \left(\frac{\hbar}{m c} \right)^2 \langle r^{-2} \rangle \left(\frac{1}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right) \right)^{\frac{1}{2}} \left\{ \kappa(\kappa \pm 1) + \frac{1}{1 - \rho^2 \langle r^{-2} \rangle} \right\} \\ = 0$$

$$\Rightarrow \pm \frac{m}{\hbar^2} \left(1 + \left(\frac{\hbar}{m c} \right)^2 \langle r^{-2} \rangle \left(\frac{1}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right) \right)^{\frac{1}{2}} = \frac{1}{2\kappa \hbar c \rho} \left\{ \kappa(\kappa \pm 1) + \frac{1}{1 - \rho^2 \langle r^{-2} \rangle} \right\} \quad (A2)$$

and

$$\frac{\partial E_{ms}}{\partial \rho} = -2\kappa \hbar c \langle r^{-2} \rangle \pm \frac{1}{2} m c^2 \left(1 + \left(\frac{\hbar}{m c} \right)^2 \langle r^{-2} \rangle \left(\frac{1}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right) \right)^{\frac{1}{2}} \left(\frac{\hbar}{m c} \right)^2 \frac{\rho \langle r^{-2} \rangle}{(1 - \rho^2 \langle r^{-2} \rangle)^2} \\ = 0 \\ \Rightarrow \pm \frac{m}{\hbar^2} \left(1 + \left(\frac{\hbar}{m c} \right)^2 \langle r^{-2} \rangle \left(\frac{1}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right) \right)^{\frac{1}{2}} = \frac{1}{4\kappa \hbar c \langle r^{-2} \rangle} \frac{\rho \langle r^{-2} \rangle^2}{(1 - \rho^2 \langle r^{-2} \rangle)^2} \quad (A3)$$

Comparing (A2) with (A3) we obtain

$$2 \left\{ \kappa(\kappa \pm 1) + \frac{1}{(1 - \rho^2 \langle r^{-2} \rangle)} \right\} = \frac{\rho^2 \langle r^{-2} \rangle}{(1 - \rho^2 \langle r^{-2} \rangle)^2}$$

Introducing $u \equiv 1 - \rho^2 \langle r^{-2} \rangle$ we have

$$u = \frac{-2 \pm (4 + 16\kappa(\kappa \pm 1))^{\frac{1}{2}}}{8\kappa(\kappa \pm 1)} = \frac{1}{4\kappa(\kappa \pm 1)} \left\{ -1 \pm (1 + 4\kappa(\kappa \pm 1))^{\frac{1}{2}} \right\} \\ = \frac{1}{4|\kappa|(|\kappa| + 1)} \left\{ -1 \pm (1 + 4|\kappa|(|\kappa| \pm 1))^{\frac{1}{2}} \right\} \\ = \begin{cases} \frac{1}{4|\kappa|(|\kappa| + 1)} \left\{ -1 \pm (1 + 4(|\kappa| + 1))^{\frac{1}{2}} \right\} \\ \frac{1}{4|\kappa|(|\kappa| - 1)} \left\{ -1 \pm (1 + 4(|\kappa| - 1))^{\frac{1}{2}} \right\} \end{cases} \\ = \begin{cases} \frac{1}{4|\kappa|(|\kappa| + 1)} \left\{ -1 \pm (2|\kappa| + 1) \right\} \\ \frac{1}{4|\kappa|(|\kappa| - 1)} \left\{ -1 \pm (2|\kappa| - 1) \right\} \end{cases} \\ = \begin{cases} \frac{1}{2(|\kappa| + 1)} & , & \frac{-1}{2|\kappa|} \\ \frac{1}{2|\kappa|} & , & \frac{-1}{2(|\kappa| - 1)} \end{cases}$$

But $u \equiv 1 - \rho^2 \langle r^{-2} \rangle = 1 - \frac{\langle r^{-1} \rangle^2}{\langle r^{-2} \rangle} > 0$ so the negative roots obtained above are extraneous. We thus have for u

$$u = \begin{cases} \frac{1}{2(|\kappa|+1)} & \text{taking the upper sign in} \\ \frac{1}{2|\kappa|} & \text{taking the upper sign in} \end{cases}$$

Thus we have that

$$\begin{aligned} \left(1 + \left(\frac{\hbar}{mc}\right)^2 \langle r^{-2} \rangle \left\{ \frac{1}{1 - \rho^2 \langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right\}\right)^2 &= \left(1 + \left(\frac{\hbar}{mc}\right)^2 \langle r^{-2} \rangle \left\{ \frac{1}{4} u^{-1} + |\kappa|(|\kappa| \pm 1) \right\}\right)^2 \\ &= \begin{cases} \left(1 + \left(\frac{\hbar}{mc}\right)^2 \langle r^{-2} \rangle (|\kappa|+1)(|\kappa| + \frac{1}{2})\right)^2 \\ \left(1 + \left(\frac{\hbar}{mc}\right)^2 \langle r^{-2} \rangle |\kappa|(|\kappa| - \frac{1}{2})\right)^2 \end{cases} \quad (A4) \end{aligned}$$

$$\begin{aligned} \kappa(\kappa \pm 1) + \frac{1}{(1 - \rho^2 \langle r^{-2} \rangle)^2} &= |\kappa|(|\kappa| \pm 1) + \frac{1}{4} u^{-2} \\ &= \begin{cases} (|\kappa|+1)(2|\kappa|+1) \\ |\kappa|(2|\kappa|-1) \end{cases} \quad (A5) \end{aligned}$$

$$\text{and } \frac{\rho^2 \langle r^{-2} \rangle}{(1 - \rho^2 \langle r^{-2} \rangle)^2} = \frac{1-u}{u^3} = \begin{cases} \frac{16(|\kappa|+1)^4(1 - \frac{1}{2(|\kappa|+1)})}{16(|\kappa|+1)^4} = 16(|\kappa|+1)(|\kappa|+1)^3 \\ \frac{16|\kappa|^4(1 - \frac{1}{2|\kappa|})}{16|\kappa|^4} = 16(|\kappa| - \frac{1}{2})|\kappa|^3 \end{cases} \quad (A6)$$

Squaring (A4) and substituting (A5) and (A6) into the result gives us the equations

$$\begin{aligned} \left(\frac{\hbar}{\hbar^2}\right)^2 \left(1 + \left(\frac{\hbar}{mc}\right)^2 \langle r^{-2} \rangle (|\kappa|+1)(|\kappa| + \frac{1}{2})\right)^2 &= \frac{1}{4(\hbar^2 c \rho)^2} (|\kappa|+1)^2 (2|\kappa|+1)^2 \\ &= \frac{1}{16 \hbar^2 c \rho^2} (|\kappa|+1)^2 (|\kappa| + \frac{1}{2})^2 \\ \Rightarrow \rho^2 &= \frac{1}{(\hbar^2 c)^2} \left(\frac{\hbar}{mc}\right)^2 (|\kappa|+1)^2 (|\kappa| + \frac{1}{2})^2 \left(1 - \frac{(\frac{\hbar}{mc})^2 \langle r^{-2} \rangle (|\kappa|+1)(|\kappa| + \frac{1}{2})}{1 + (\frac{\hbar}{mc})^2 \langle r^{-2} \rangle (|\kappa|+1)(|\kappa| + \frac{1}{2})}\right) \\ &= \frac{1}{(\hbar^2 c)^2} \left(\frac{\hbar}{mc}\right)^2 (|\kappa|+1)^2 (|\kappa| + \frac{1}{2})^2 \left(1 - (4 \hbar^2 c)^2 \frac{\langle r^{-2} \rangle (|\kappa|+1)(|\kappa| + \frac{1}{2})}{\rho^2 \langle r^{-2} \rangle}\right) \\ &= \frac{1}{(\hbar^2 c)^2} \left(\frac{\hbar}{mc}\right)^2 (|\kappa|+1)^2 (|\kappa| + \frac{1}{2})^2 (1 - 16 \hbar^2 c)^2 \frac{(|\kappa|+1)(|\kappa| + \frac{1}{2})}{16(|\kappa|+1)(|\kappa|+1)^3} \end{aligned}$$

$$= \frac{1}{(2\epsilon)^2} \left(\frac{\hbar}{mc} \right)^2 (|\kappa| + \frac{1}{2})^2 ((|\kappa| + 1)^2 - (2\epsilon)^2)$$

$$\Rightarrow \rho = \frac{1}{2\epsilon} \left(\frac{\hbar}{mc} \right) (|\kappa| + \frac{1}{2}) ((|\kappa| + 1)^2 - (2\epsilon)^2)$$

$$\begin{aligned} \langle r^{-2} \rangle &= \frac{1-4}{\rho^2} = \left(\frac{2\epsilon}{\hbar/mc} \right)^2 (|\kappa| + \frac{1}{2})^{-2} ((|\kappa| + 1)^2 - (2\epsilon)^2)^{-1} \left(1 - \frac{1}{2(|\kappa| + 1)} \right) \\ &= \left(\frac{2\epsilon}{\hbar/mc} \right)^2 (|\kappa| + \frac{1}{2})^{-1} (|\kappa| + 1)^{-1} ((|\kappa| + 1)^2 - (2\epsilon)^2)^{-1} \end{aligned}$$

and

$$\begin{aligned} \left(\frac{m}{\hbar^2} \right)^2 \left\{ 1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle |\kappa| (|\kappa| - \frac{1}{2}) \right\} &= \frac{1}{4(2\epsilon \hbar c \rho)^2} |\kappa|^2 (2|\kappa| - 1)^2 \\ &= \frac{1}{(2\epsilon \hbar c \rho)^2} |\kappa|^2 (|\kappa| - \frac{1}{2})^2 \end{aligned}$$

$$\begin{aligned} \Rightarrow \rho^2 &= \frac{1}{(2\epsilon)^2} \left(\frac{\hbar}{mc} \right)^2 |\kappa|^2 (|\kappa| - \frac{1}{2})^2 \left(1 - \frac{\left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle |\kappa| (|\kappa| - \frac{1}{2})}{1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle |\kappa| (|\kappa| - \frac{1}{2})} \right) \\ &= \frac{1}{(2\epsilon)^2} \left(\frac{\hbar}{mc} \right)^2 |\kappa|^2 (|\kappa| - \frac{1}{2})^2 \left(1 - (4\epsilon)^2 \frac{\langle r^{-2} \rangle |\kappa| (|\kappa| - \frac{1}{2})}{\frac{\rho^2 \langle r^{-2} \rangle^2}{(1 - \rho^2 \langle r^{-2} \rangle)^4}} \right) \\ &= \frac{1}{(2\epsilon)^2} \left(\frac{\hbar}{mc} \right)^2 |\kappa|^2 (|\kappa| - \frac{1}{2})^2 \left(1 - (4\epsilon)^2 \frac{|\kappa| (|\kappa| - \frac{1}{2})}{16 (|\kappa| - \frac{1}{2}) |\kappa|^3} \right) \\ &= \frac{1}{(2\epsilon)^2} \left(\frac{\hbar}{mc} \right)^2 (|\kappa| - \frac{1}{2})^2 (|\kappa|^2 - (2\epsilon)^2) \end{aligned}$$

$$\Rightarrow \rho = \frac{1}{2\epsilon} \frac{\hbar}{mc} (|\kappa| - \frac{1}{2}) (|\kappa|^2 - (2\epsilon)^2)^{\frac{1}{2}} = \frac{\hbar/mc}{2\epsilon} (|\kappa| - \frac{1}{2}) Y$$

$$\begin{aligned} \langle r^{-2} \rangle &= \frac{1-4}{\rho^2} = \left(\frac{2\epsilon}{\hbar/mc} \right)^2 (|\kappa| - \frac{1}{2})^{-2} (|\kappa|^2 - (2\epsilon)^2)^{-1} \left(1 - \frac{1}{2|\kappa|} \right) \\ &= \left(\frac{2\epsilon}{\hbar/mc} \right)^2 |\kappa|^{-1} (|\kappa| - \frac{1}{2})^{-1} (|\kappa|^2 - (2\epsilon)^2)^{-1} \\ &= \left(\frac{2\epsilon}{\hbar/mc} \right)^2 Y^{-1} |\kappa|^{-1} (|\kappa| - \frac{1}{2})^{-1} \end{aligned}$$

Thus

$$\begin{aligned}
 E_{ms} &= -Z\alpha\hbar c\rho\langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle \left\{ \frac{1}{1-\rho^2\langle r^{-2} \rangle} + \kappa(\kappa \pm 1) \right\} \right)^{\frac{1}{2}} \\
 &= \left\{ \begin{aligned} &-Z\alpha\hbar c\rho\langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle \left\{ \frac{1}{4} \psi^{-1} + |\kappa|(|\kappa|+1) \right\} \right)^{\frac{1}{2}} \\ &-Z\alpha\hbar c\rho\langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle \left\{ \frac{1}{4} \psi^{-1} + |\kappa|(|\kappa|-1) \right\} \right)^{\frac{1}{2}} \end{aligned} \right\} \\
 &= \left\{ \begin{aligned} &-Z\alpha\hbar c\rho\langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle (|\kappa|+1)(|\kappa|+\frac{1}{2}) \right)^{\frac{1}{2}} \\ &-Z\alpha\hbar c\rho\langle r^{-2} \rangle \pm mc^2 \left(1 + \left(\frac{\hbar}{mc} \right)^2 \langle r^{-2} \rangle |\kappa|(|\kappa|-\frac{1}{2}) \right)^{\frac{1}{2}} \end{aligned} \right\} \\
 &= \left\{ \begin{aligned} &mc^2 \left\{ -(\frac{Z\alpha}{|\kappa|})^2 \left(1 - \left(\frac{Z\alpha}{|\kappa|+1} \right)^2 \right)^{-\frac{1}{2}} \pm \left(1 + (\frac{Z\alpha}{|\kappa|+1})^2 - (\frac{Z\alpha}{|\kappa|})^2 \right)^{-\frac{1}{2}} \right\} \\ &mc^2 \left\{ -(\frac{Z\alpha}{|\kappa|})^2 \left(1 - \left(\frac{Z\alpha}{|\kappa|} \right)^2 \right)^{-\frac{1}{2}} \pm \left(1 + (\frac{Z\alpha}{|\kappa|})^2 - (\frac{Z\alpha}{|\kappa|})^2 \right)^{-\frac{1}{2}} \right\} \end{aligned} \right\} \\
 &= \left\{ \begin{aligned} &mc^2 \left((|\kappa|+1)^2 - (\frac{Z\alpha}{|\kappa|})^2 \right)^{-\frac{1}{2}} \left(-\frac{(\frac{Z\alpha}{|\kappa|})^2}{|\kappa|+1} \pm (|\kappa|+1) \right) \\ &mc^2 \left(|\kappa|^2 - (\frac{Z\alpha}{|\kappa|})^2 \right)^{-\frac{1}{2}} \left(-\frac{(\frac{Z\alpha}{|\kappa|})^2}{|\kappa|} \pm |\kappa| \right) \end{aligned} \right\} \\
 &= \left\{ \begin{aligned} &mc^2 \frac{((|\kappa|+1)^2 - (\frac{Z\alpha}{|\kappa|})^2)^{\frac{1}{2}}}{|\kappa|+1} = mc^2 \left(1 - \left(\frac{Z\alpha}{|\kappa|+1} \right)^2 \right)^{\frac{1}{2}} \\ &-mc^2 \frac{1 + \left(\frac{Z\alpha}{|\kappa|+1} \right)^2}{\left(1 - \left(\frac{Z\alpha}{|\kappa|+1} \right)^2 \right)^{\frac{1}{2}}} \\ &mc^2 \frac{1}{|\kappa|} \\ &-mc^2 \frac{1 + \left(\frac{Z\alpha}{|\kappa|} \right)^2}{\left(1 - \left(\frac{Z\alpha}{|\kappa|} \right)^2 \right)^{\frac{1}{2}}} \end{aligned} \right\}
 \end{aligned}$$

Now, from our analytic expressions for the eigenenergies and eigenstates we have that

$$E_{j,l} = mc^2 \left(1 + \left(\frac{Z\alpha}{\gamma+1} \right)^2 \right)^{-\frac{1}{2}}$$

and thus the ratio of the analytic energy of the first excited bound-state to the Mark-Schwarz value is given by

$$\begin{aligned}
 \left(1 + \left(\frac{Z\alpha}{\gamma+1}\right)^2\right)^{-\frac{1}{2}} \left(1 - \left(\frac{Z\alpha}{|\kappa|+1}\right)^2\right)^{-\frac{1}{2}} &= \left(1 + (Z\alpha)^2 \left[\frac{1}{(\gamma+1)^2} - \frac{1}{(|\kappa|+1)^2}\right] - \frac{(Z\alpha)^4}{(\gamma+1)^2(|\kappa|+1)^2}\right)^{-\frac{1}{2}} \\
 &= \left(1 + (Z\alpha)^2 \frac{|\kappa|^2 + 2|\kappa| - \gamma^2 - 2\gamma}{(\gamma+1)^2(|\kappa|+1)^2} - \frac{(Z\alpha)^4}{(\gamma+1)^2(|\kappa|+1)^2}\right)^{-\frac{1}{2}} \\
 &= \left(1 + \frac{2(|\kappa| - \gamma)(Z\alpha)^2}{(\gamma+1)^2(|\kappa|+1)^2}\right)^{-\frac{1}{2}} \\
 &< 1
 \end{aligned}$$

Therefore the energy obtained by the Mark-Schwarz method for the first excited bound-state does in fact exceed the analytic value.

The ground state is given analytically by

$$\begin{aligned}
 q(r) &= N r^\gamma e^{-\lambda r}, \quad N \equiv \left(\frac{\Gamma(2\gamma+1)}{(2\lambda)^{2\gamma+1}}\right)^{-\frac{1}{2}} \\
 \Rightarrow \langle r^{-1} \rangle &= \frac{(2\lambda)^{2\gamma+1}}{\Gamma(2\gamma+1)} \frac{\Gamma(2\gamma)}{(2\lambda)^{2\gamma}} = \lambda/\gamma = \frac{Z\alpha}{\hbar/mc} \frac{\gamma^{-1}}{|\kappa|} \\
 \langle r^{-2} \rangle &= \frac{(2\lambda)^{2\gamma+1}}{\Gamma(2\gamma+1)} \frac{\Gamma(2\gamma-1)}{(2\lambda)^{2\gamma-1}} = \frac{\lambda^2}{\gamma(\gamma-\frac{1}{2})} = \left(\frac{Z\alpha}{\hbar/mc}\right)^2 \frac{\gamma^{-1}(\gamma-\frac{1}{2})^{-1}}{|\kappa|^2} \\
 \rho &\equiv \frac{\langle r^{-1} \rangle}{\langle r^{-2} \rangle} = \frac{\hbar/mc}{Z\alpha} |\kappa| (\gamma - \frac{1}{2})
 \end{aligned}$$

Thus while the Mark-Schwarz approximation to the ground-state eigenfunction gives the expectation of r^{-1} exactly, the value yielded for ρ differs from the exact value by a factor of γ , which will result in a considerable discrepancy for large atomic numbers, where a relativistic treatment is of greatest relevance.

Thus we see in this analysis for a four-dimensional variational subspace that while the Mark-Schwartz method gives the exact Dirac eigenenergies for $K < 0$ states, the corresponding eigenfunctions differ from the exact eigenfunctions, and this discrepancy increases with increasing atomic number. Moreover, while the system is constrained to give the exact eigenenergies in the non-relativistic limit for electronic systems, reversal of the sign of the potential merely reverses the signs of the eigenenergies obtained, resulting in incorrect energies for positrons in the non-relativistic limit.

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20. Please note that the Einstein summation convention is followed throughout this paper.

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